NASA Technical Memorandum 78761

MODIFIED COMPOSITE MATERIALS WORKSHOP

Dennis L. Dicus, Compiler

JULY 1978

DEPARTMENT OF DEFENSE PLASTICS TECHNICAL EVALUATION CENTER ARRADCOM, DOVER, N. J. 07801

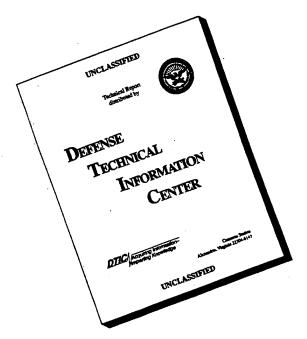


National Aeronautics and Space Administration

Langley Research Center Hampton, Virginia 23665 DTIC QUALITY INSPECTED 1

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MODIFIED COMPOSITE MATERIALS

WORKSHOP

(Held at Langley Research Center, Hampton, Virginia, March 23-24, 1978)

DENNIS L. DICUS, Compiler

JULY 1978

PREFACE

A hazard which results from accidental release of graphite fibers from composite materials has been identified. The risk resulting from this hazard is being evaluated. In the meantime, NASA has initiated a program to explore alternate materials which eliminate the hazard or reduce the risk. On March 23 and 24, 1978, NASA Langley Research Center sponsored a Modified Composite Materials Workshop. This workshop was intended to display the NASA program on alternate materials and to solicit new ideas for other alternate materials.

Working groups were organized to consider six topics: epoxy modifications, epoxy replacement, fiber modifications, fiber coatings and new fibers, hybrids, and fiber release testing. Because of the time required to develop a new material and acquire a design data base, most of the workers concluded that a modified composite material would require about four to five years of development and testing before it could be applied to aircraft structures. However, the Hybrid Working Group considered that some hybrid composites which reduce the risk of accidental fiber release might be put into service over the near term. The Fiber Release Testing Working Group recommended a coordinated effort to define a suitable laboratory test. That group did not have sufficient time to give careful consideration to the problems of large scale outdoor testing to prove the performance at full scale of proposed alternate materials. Most groups expressed a desire for further interaction with NASA in their technology areas in the future to monitor progress.

Hampton, Virginia July 11, 1978

General Chairman

Willam A. Brooks, Jr. - NASA Langley Research Center

Administrative Chairman

Dennis L. Dicus - NASA Langley Research Center

Program Co-Chairmen

Robert T. Swann - NASA Langley Research Center Norman J. Johnston - NASA Langley Research Center

Working Group Chairmen

E. Bruce Belason - AVCO Specialty Materials Division
Russell J. Diefendorf - Rensselaer Polytechnic Institute
James Economy - IBM Research Laboratory
Billy F. Landrum - Ciba-Geigy Corporation
James Noland - American Cyanamid Company
Karl M. Prewo - United Technologies Research Center

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INTRODUCTION

Graphite fibers in an epoxy matrix provide a composite material having high strength and stiffness relative to its weight. Because low weight is such an important consideration in aircraft structures, NASA has undertaken a variety of activities intended to resolve problems involved in applying these composite materials to aircraft structures. NASA activities include laboratory studies, as well as major projects to get flight experience with composites in secondary and primary structures on commercial aircraft. However, because of their low density, small diameter, and high electrical conductivity, graphite fibers raise issues beyond those normally considered in structural design.

Since graphite fibers are electrical conductors, they can cause short circuits, equipment malfunctions, or possibly fires if they get into electrical equipment. Furthermore, because of their low density and small diameter, graphite fibers can remain airborne for considerable time, and hence can be transported from the scene of electrical or electronic equipment. NASA has underway a project to study, and if possible, to quantify the risk associated with this electrical hazard. While no definitive results from this risk assessment study will be available for some time, NASA has initiated exploratory investigations of alternate materials which can reduce electrical hazards and yet retain or enhance currently available graphite fiber composites properties.

On March 22 and 23, 1978, NASA Langley Research Center held a workshop to display the current program on alternate materials, to solicit approaches other than those being investigated, and to stimulate further thinking about possible materials solutions to eliminate a possible electrical hazard. At the workshop, a brief overview of the risk assessment activity was provided. This overview was not intended to be complete or definitive, nor was the workshop intended to address risk issues except from the point of view of alternate materials which would tend to reduce risk. After the risk overview, Langley, Lewis, and Ames Research Centers presented summaries of programs and plans to explore alternate materials. Following these summaries, test methods currently used to study accidental graphite fiber release were outlined. After the discussion of test methods, attendees divided into six working groups.

The workshop had working groups on epoxy modifications, epoxy replacement, fiber modifications, fiber coatings and new fibers, hybrids, and fiber release testing. These working

groups began with prepared presentations in their topic areas. Then they considered a set of issues that had been defined in advance. After further deliberations, the working groups prepared reports, guided by a recommended format, which were presented to all attendees. For each working group, two NASA employees were assigned as reporters, and they provided summaries of the activities of the groups.

The purpose of this document is to provide to attendees and other interested persons as much information as is likely to be useful and can be readily compiled. No text is available for any of the presentations. The information contained in this document includes copies of vugraphs used in presenting NASA programs, vugraphs summarizing working group findings, and NASA reporters' accounts of working group Also included are an attendance list, and issues activities. directed to each group. While care has been exercised in compiling this information, editing has been minimal and the source of the information should be consulted before taking further action. Furthermore, the reporter's accounts of the working group proceedings reflect the reporter's view of a dynamic process, and the opinions expressed may not reflect the considered judgement of the individuals involved or of their sponsoring institutions.

- A Report of Observed Effects on Electrical Systems of Airborne Carbon/Graphite Fibers. NASA TM 78652, 1978.
- Intergovernmental Committee, Compilers: Carbon Fiber Study. NASA TM 78718, 1978.

AGENDA

MODIFIED COMPOSITE MATERIALS WORKSHOP

March 23-24, 1978 NASA-Langley Research Center Hampton, Virginia

Thursday, March 23

8:00 a.m. Registration

8:30 Welcome Richard R. Heldenfels

NASA-Langley

Workshop Expectations William A. Brooks, Jr.

NASA-Langley

Potential Graphite Fiber Problems Vernon L. Bell NASA-Langley

Review of NASA-Langley Materials Modification Program

Overview Robert T. Swann NASA-Langley

Improved High Modulus Fibers R. J. Diefendorf

Rensselaer Polytechnic

Institute

Graphite Fibers with High Elec-

trical Resistivity

Silicon Carbide, Boron, and Glass Coated Graphite Fibers

Boron Carbide and Silicon Carbide Coated Graphite Fibers

Boron Nitride, Silicon Carbide and Silicone Coated Graphite Fibers

Raymond Suplinskas AVCO Corporation

F. Lincoln Vogel

Francis Galasso

Un. of Pennsylvania

United Technologies Research Center

Herbert F. Volk Union Carbide Corporation

10:35-10:50 BREAK

10:50 Review of NASA-Ames Materials Modification Program

An Approach to the Development of Fire Resistant Composites

Preliminary Test Results of the Fiber Release Characteristics of Baseline Graphite Epoxy Compos-

ites Compared with New Char Forming Analogs John A. Parker NASA-Ames

Joseph Mansfield

NASA-Ames

Review of NASA-Lewis Materials Modification Program

Tito T. Serafini NASA-Lewis

12:10 - - .0 .m. - LUNCH - NASA Cafeteria (B-1213) Private Dining Ref

1:10 p.m.	Fiber Release Testing Facilities and Results	Vernon L. Bell NASA-Langley
1:40	Charge to Working Groups	
1:50	Working Groups Convene (6 concurrent mee	tings)
	I. Graphite Fiber ModificationR. J. Diefendorf, ChairmanRensselaer Polytechnic Institute	STAGE
	II. Graphite Fiber Coating and Alterna James Economy, Chairman IBM Research Laboratory	tive Fibers HAMPTON ROOM
	III. Epoxy Resin Modifications James Noland, Chairman American Cyanamid Company	SUN LOUNGE
	<pre>IV. Epoxy Resin Replacements B. F. Landrum, Chairman Ciba-Geigy Corporation</pre>	MAIN LOUNGE
	V. Hybrid Composites Karl Prewo, Chairman United Technologies Research Cente	WYTHE ROOM
	VI. Fiber Release Simulation Testing E. Bruce Belason, Chairman AVCO Corporation	LANGLEY ROOM
2:00-3:00	Coffee or Soft Drinks will be available	in Main Lounge
5:00	Working Groups Recess Buses depart for Holiday Inn	
6:00	Buses depart Holiday Inn for Sam's Seafo	od Restaurant
6:15	Cash Bar Social	
7:00	Dinner	
	Friday, March 24	
8:00 a.m.	Working Groups Reconvene	•
9:45	BREAK	
10:00	Reassemble for Working Group Reports	
12:30 p.m	Closing Remarks	
12:45	Buses depart for Patrick Henry Internati Holiday Inn	onal Airport and

WORKSHOP EXPECTATIONS

WILLIAM A. BROOKS, JR. MARCH 23, 1978

MODIFIED COMPOSITE MATERIALS WORKSHOP NASA LANGLEY RESEARCH CENTER MARCH 23-24, 1978

OBJECTIVES

- DISPLAY NASA PROGRAM ON MATERIALS MODIFICATIONS TO ALLEVIATE POTENTIAL ELECTRICAL PROBLEMS WITH GRAPHITE FIBER COMPOSITES 0
- SOLICIT POSSIBLE SOLUTIONS TO THIS PROBLEM FROM THE COMPOSITE MATERIALS COMMUNITY 0
- INITIATE A MORE GENERAL INVOLVEMENT OF THE COMPOSITES MATERIALS COMMUNITY IN APPROPRIATE ACTIVITIES 0

MODIFIED COMPOSITE MATERIALS WORKSHOP NASA LANGLEY RESEARCH CENTER MARCH 23-24, 1978

PARTICIPATION

	INVITATIONS	ACCEPTANCES
INDIVIDUALS (POLYMERS, FIBERS, FIRE TESTING)	149	111
COMMERCIAL COMPANIES	9	51
UNIVERSITIES	10	9
GOVERNMENT INSTALLATIONS	56	21

POTENTIA

GRAPHITE

IBER

PROBLEMS

GRAPHITE COMPOSITES

- O IMPORTANT LIGHTWEIGHT STRUCTURAL MATERIAL
- O USED CURRENTLY IN AEROSPACE, SPORTING GOODS
- O RAPID GROWTII PROJECTED

AEROSPACE: 1 MILLION LBS. (1990)
AUTOMOTIVE: 1 BILLION LBS. (1990)

1 MILLION LBS, (1990)

CONSUMER PRODUCTS:

O MADE UP OF LIGHT GRAPHITE FIBERS IN POLYMER MATRIX

COMMERCIAL AIRCRAFT COMPOSITES CF 0 F USES

PRESENT

13 LBS. CF/PLANE 30 LBS. CF/PLANE 25 B-747's WITH CF/EPOXY FLOORS 28 B-737's WITH 4 SPOILERS 7 DC-10's SPOILERS: RUDDERS: FLOORS:

FUTURE

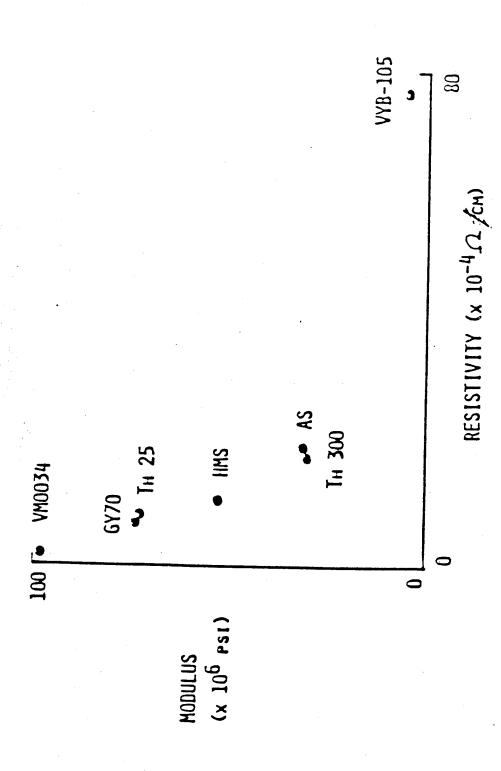
125 LBS. CF 700 LBS. CF 700 LBS. 70 LBS. CF 40 LBS, CF 130 LBS, CF 737 HORIZONTAL STABILIZER SECONDARY STRUCTURE L-1011 VERTICAL FIN" DC-10 VERTICAL FIN PRIMARY STRUCTURE L-1011 AILERON 727 ELEVATOR DC-10 RUDDER

5

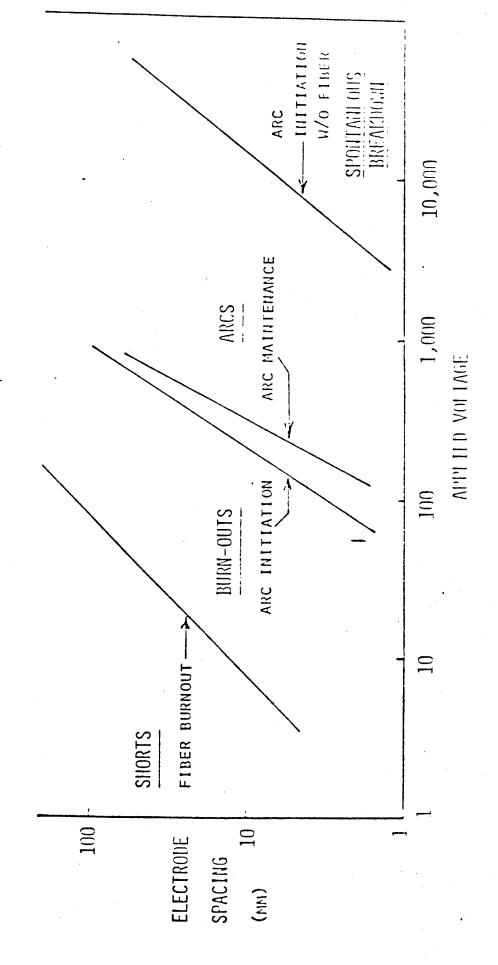
BERS GRAPH 日0 SOI CHARACTERIST

- HIGH MODULUS (~50 X 10⁶ PSI)
- DIAMETER (~8 MICRONS)
- FALL RATE (~2 CM/SEC)
- RESISTIVITY ($\sim 1000 \Omega$ CM)
- FIBER BURNOUT 0.5 TO 1 WATT/CM (~10 To 30 MA)
- CONTACT VOLTAGE DROP (~2 To 5 VOLTS)

RESISTIVITY N O MODULUS EFFECT OF



EFFECTS FIBER ELECTRICAL GRAPHITE 0 F SUMMARY



- CRASH AND FIRE
- o INDUSTRIAL OPERATIONS
- o SCRAP/WASTE DISPOSAL
- o INCINERATION OF USED PRODUCTS
- o TESTING

STRUCTURES GRAPHITE F 0 R ANALYSIS RISK

OBJECTIVES

SHORT TERM

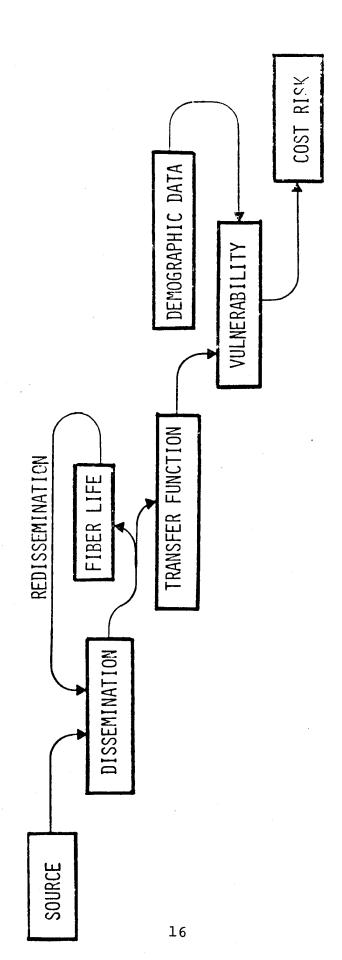
ESTABLISH LEVEL OF CONFIDENCE IN METHODS AND RESULTS

QUANTIFY NEAR TERM RISK OF GRAPHITE FIBER ON CURRENT CIVIL AIRCRAFT

LONG TERM

QUANTIFY RISKS ASSOCIATED WITH ACCIDENTAL RELEASE OF GRAPHITE FIBERS FROM AERONAUTICAL USES OF COMPOSITES IN THE FUTURE

REDUCTION IN RISKS ASSOCIATED WITH USE OF MODIFIED MATERIALS QUANTIFY



DURCE PARAMETERS

AIRCRAFT ACCIDENT AND FIRE STATISTICS

AIRCRAFT ACCIDENT AND FIRE LOCATIONS

FIRE ENERGY CONTENT AND RATE

FIRE FIGHTING EFFECTS

. 17. QUANTITY AND LENGTHS RELEASED

DISSEMINATION PARAMETERS

ATMOSPHERICS .

STABILITY

WIND

INVERSION HEIGHT

HEATHER

FALL VELOCITY OF FIBER

LENGTH DEPENDENCE

LOCAL EFFECTS

FIRE PLUME

TURBULENCE, VORTICES

BUILDINGS, TREES

LIFE AND REENTRAINMENT

TRANSFER FUNCTION PARAMETER

PARAMETERS: Fiber Length
Fiber Fall Velocity
Local Velocity
Season (DOORS, WINDOWS, CANOPIES)
Case OPENING AREA

BUILDINGS, ROOMS, AIRCRAFT, EQUIPMENT RACKS, AIR CONDITIONING, FILTERS . . REQUIRED FOR:

Farmon Con Any

VULNERABILITY

USER CLASSIFICATIONS:

HOME APPLIANCES

COMMERCIAL

MANUFACTURE

PUBLIC SERVICE.

POLICE, FIRE, COMMUNICATIONS

AIRCRAFT

IYPE CLASSIFICATIONS:

20

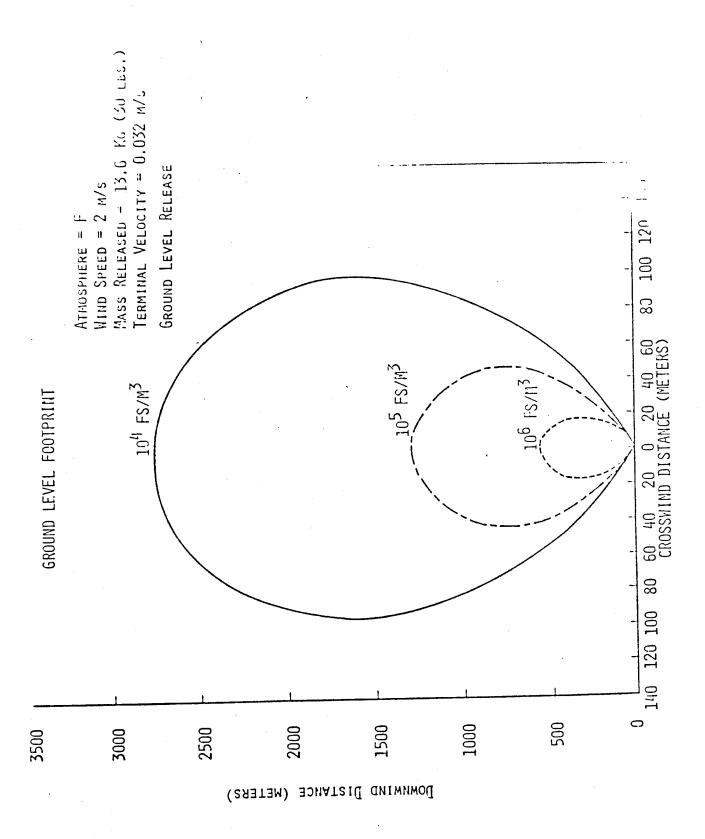
Motors

AMPLIFIERS

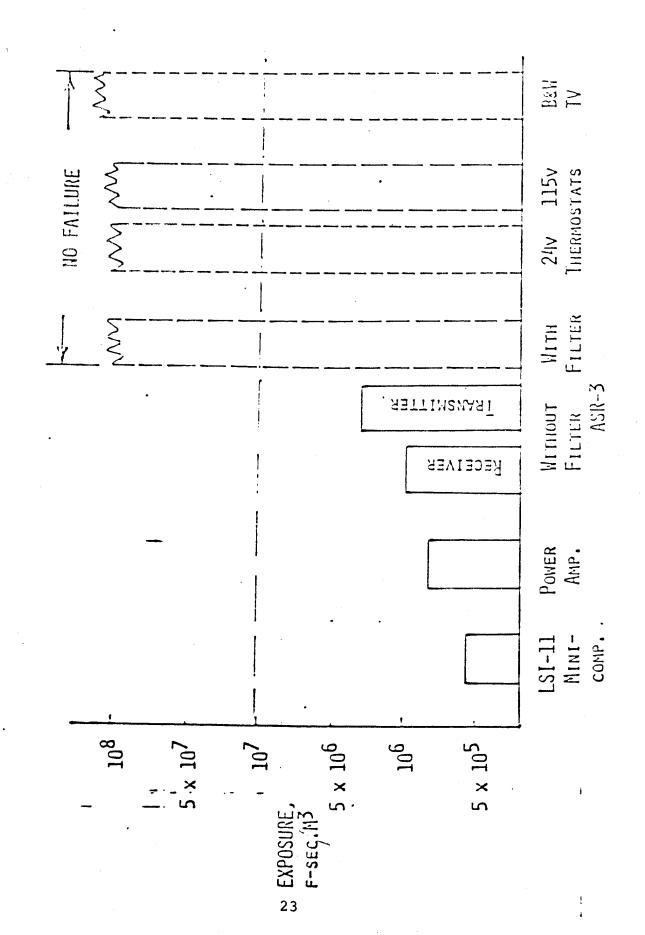
CONTROLLERS

Radars

% Mc Released 38 20 5.2×10^8 1.8×10^8 FIBERS/LB RELEASE CHARACTERISTICS TESTS 20 10 MIN 1 MIN CHAMBER TIME 16 LENGTH, MM BT67/X44 BT120/90 TEST EXPLODE ∞ BURNAND MATERIAL 108 106 107 7 Ŋ 2 FIBERS/LB LENGTH) (Per MM BURNED



EOUIPMENT CIVILIAN F 0 R LEVELS EXPOSURE FAILURE



CONCLUSIONS

- Preliminary computations indicate the risk is neither negligible nor of high MAGNITUDE, HOWEVER,
- INSUFFICIENT DATA IS AVAILABLE TO ADEQUATELY COMPUTE THE MAGNITUDE OF THE RISK 2.
- 3. FURTHER WORK IS REQUIRED:
- TEST DATA IS REQUIRED ON SOURCES, TRANSFER FUNCTION AND VULNERABILITY
 - B. MODELLING FOR THESE FACTORS IS REQUIRED
- METHODOLOGY FOR COMPUTING AND PREDICTING RISK NEEDS DEVELOPMENT

OVERVIEW

NASA LANGLEY MATERIALS MODIFICATION PROGRAM

ROBERT T. SWANN MARCH 23, 1978

IMPROVED MATERIALS FOR STRUCTURAL COMPOSITES

LANGLEY RESEARCH CENTER PROGRAM

PRIMARY PROGRAM

FIBER MODIFICATIONS

RPI U. PA - MERADCOM

FIBER COATINGS

UTRC AVCO UNION CARBIDE

SECONDARY PROGRAM

ALTERNATE FIBERS (BN) SOURCE PENDING

HYBRIDS

RESIN MODIFICATIONS

IMPROVED MATERIALS FOR STRUCTURAL COMPOSITES

HYBRIDS AND RESIN MODIFICATIONS

SCREEN HYDBRIDS AND RESIN MODIFICATIONS TO DETERMINE WHICH ONES REDUCE FIBER RELEASE OBJECTIVE:

EVALUATE HYBRIDS APPROACH:

OUTER PLIES WITH S-GLASS AND E-GLASS FIBERS OUTER PLIES WITH BORON FIBERS METAL CLADDING ADD SEALING GLASS

EVALUATE RESIN MODIFICATIONS

NCNS: EPOXY

XYLOK; EPOXY SILICONE; EPOXY HEXCEL 178 PI

IMPROVED MATERIALS FOR STRUCTURAL COMPOSITES

ALTERNATE FIBERS

DEVELOP HIGH STRENGTH, HIGH MODULUS BORON NITRIDE FIBERS OBJECTIVE:

COOPERATE WITH NAVY TO EXTEND USAF-INITIATED DEVELOPMENT OF BN FIBERS 0 APPROACH:

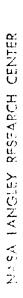
DEVELOP TECHNICAL PLAN WHICH ADDRESSES CRITICAL PROBLEMS IDENTIFIED IN PRIOR WORK

0

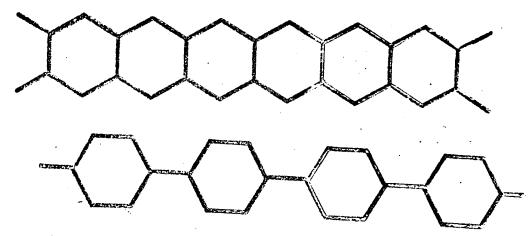
IMPROVED HIGH MODULUS FIBER

R. J. DIEFENDORF RENSSELAER POLYTECHNIC INSTITUTE

MARCH 23, 1978



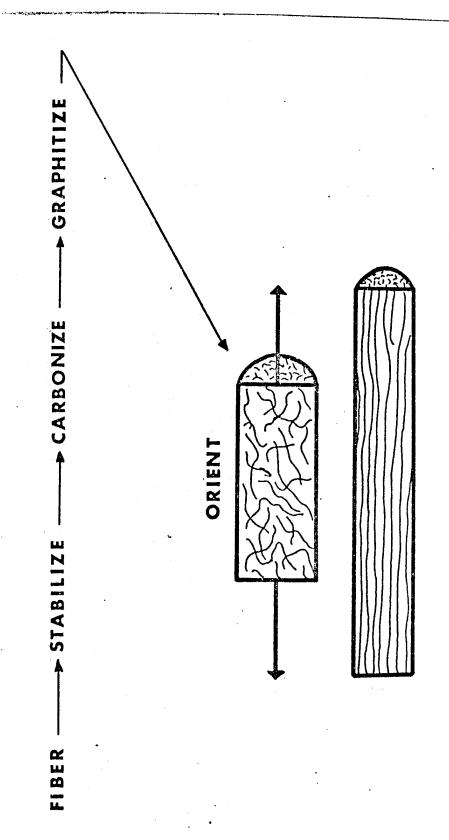
LADDER POLYMERS



- 1) M.P. TOO HIGH
- 2) INSOLUBLE

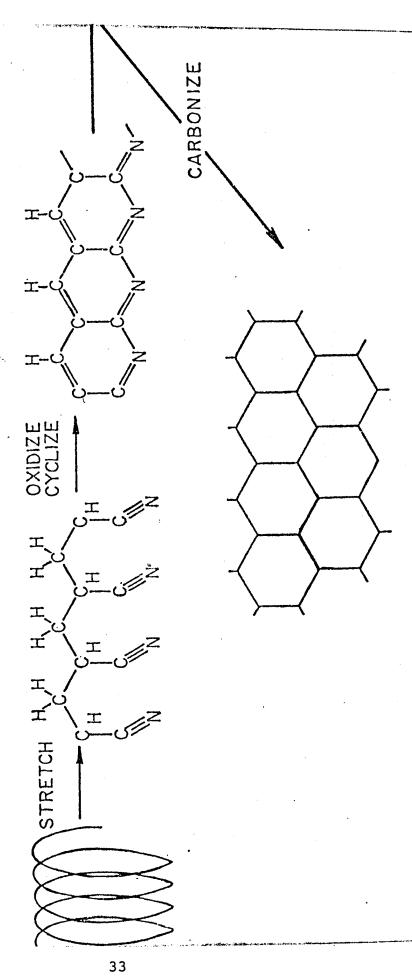
KEVLAR

- D) AMIDE GROUPS MAKE SOLUBLE
- 2) FORMS L.C.

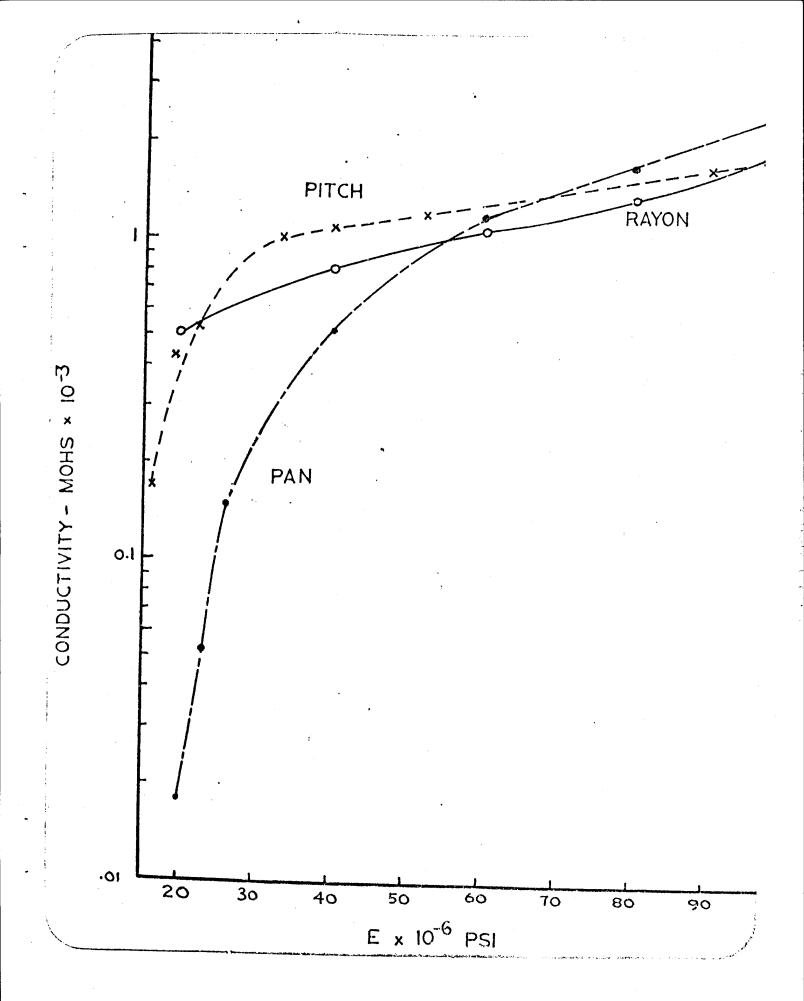


POLYACRYLONITRILE

PROCESS



PITCH FIBERS 2



SULVIIOUS.

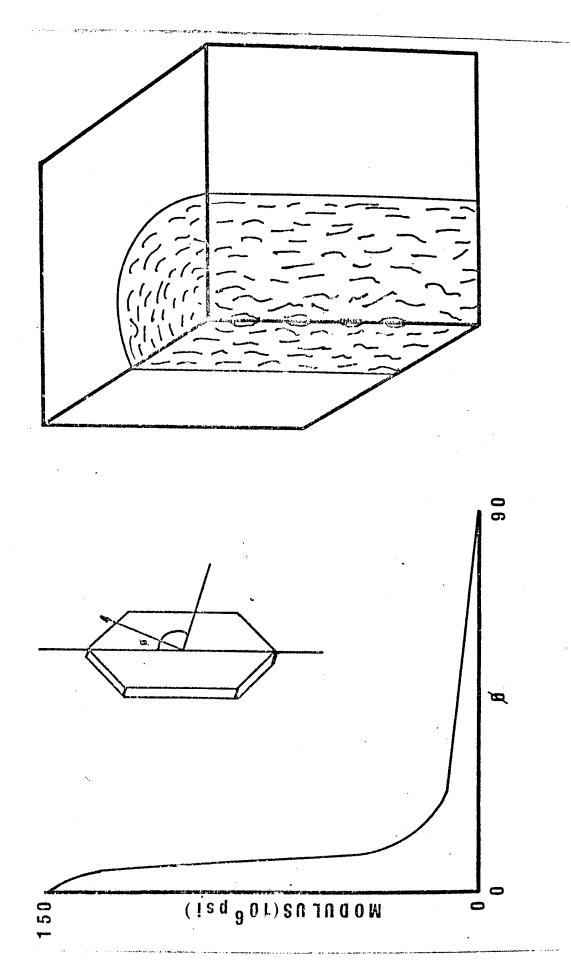
NOLLYINGHAO

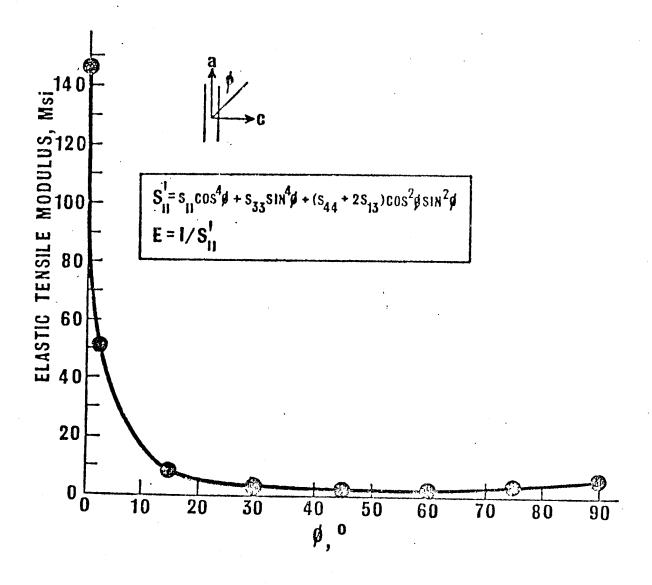
Tanille South

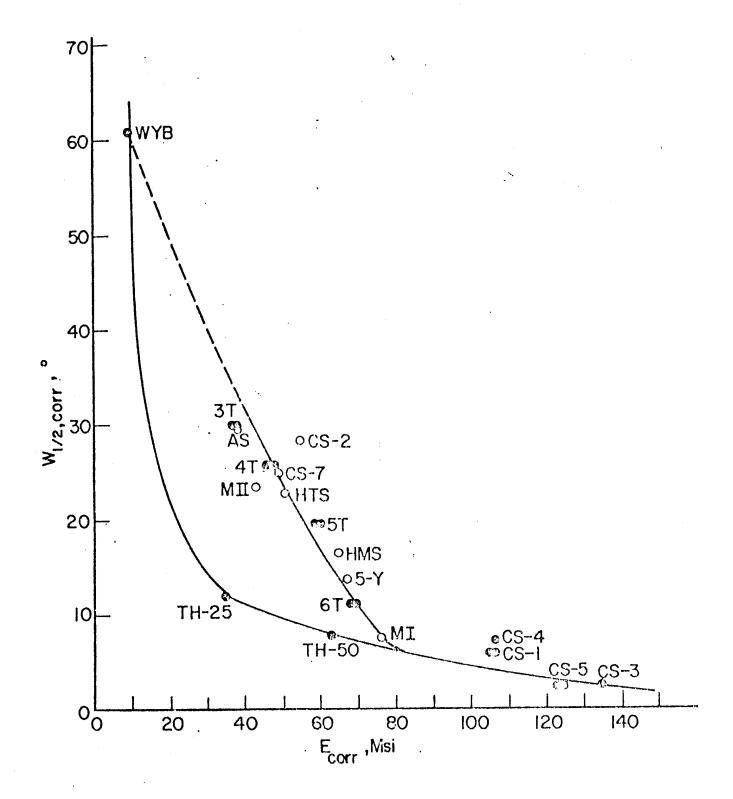
FLASTIC CONSTANTS

BOIS BAITSVASAUS.

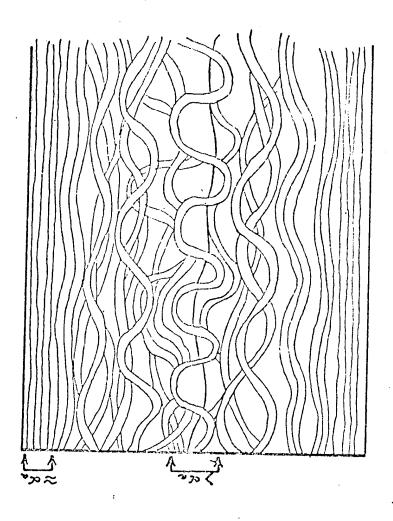
FIBER PREFERRED ORIENTATION

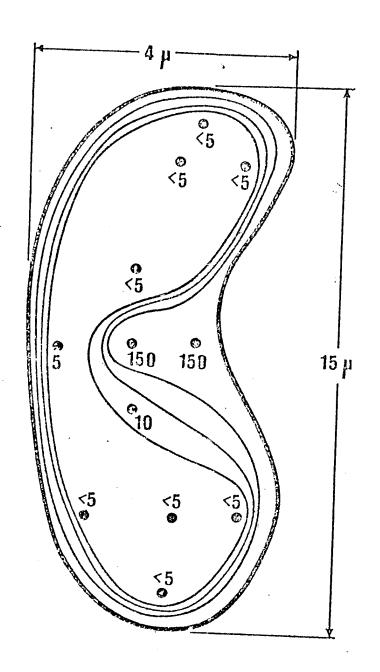






Index of Preferred Orientation, $W_{\frac{1}{2}}$ vs. Fiber Modulus



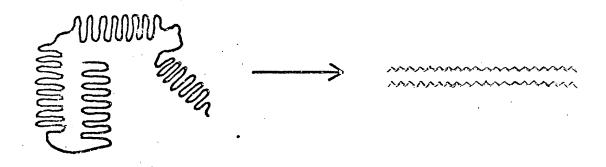


NUMBERS REPRESENT AXIAL MODULI VALUES
(IN MSI) OVER THE CROSS SECTION OF THE FIBER.

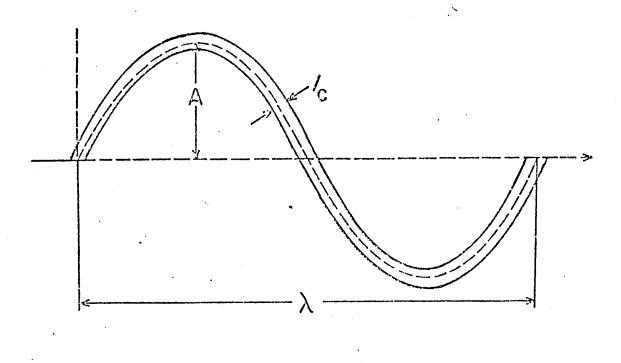
LOW TEMPERATURE DEFECTS (WORK WITH PAN AND PITCH)

- . ORIENTATION
- RELAXATION
 - OXIDATION
 - CARBONIZATION
- FIBRIL SIZE LA AND LC

FULLY EXTENDED PE.



- I. HYDROSTATIC EXTRUSION
- 2. WARM DRAWING
- 3. L.C. MELT EXTRUSION?





$$A/\lambda = 10^{-2}$$

RESISTIVITY

- . LOW TEMPERATURE DEFECTS
- . NITROGEN TRAPS PAN
- . BORON/NITROGEN/CARBON SOLID SOLUTION
- INSULATING COATING -BN SiC

PROPERTY	<u>BN</u>	<u> </u>
MELTING POINT	2400°C (SUBL.)	3600°C (subl.)
THEOR. DENSITY	2.25	2.25
ELEC. RESIST. 25°C (OHM-CM)	1013 - 1010	10^{-3}
THERM. Exp. Coef. 25°C -α _a	1.8 x 10-6	1.8×10^{-6}
THERM. Exp. Coef. 25°C $-\alpha_{c}$	45 x 10 ⁻⁵	15×10^{-6}

.

•

ABSTRACT

Graphite Fibers with High Electrical Resistivity

BY: F.L. Vogel⁺, Russell Eaton*, and W. David Lee*

Problems of arc over and circuit perturbation in electrical equipment have been traced to the presence of graphite fibers. A potential solution to this problem lies in increasing the electrical resistivity of the graphite fibers by several orders of magnitude. It is proposed herein that this may be accomplished by treating the fibers to form graphitic oxide. This treatment has the effect of inserting oxygen into the graphite lattice and increasing the resistivity considerably. The graphite layer planes remain largely unaffected and so the elastic modulus and tensile strength are predicted to be unchanged.

Supporting work in the literature will be reviewed,

- Department of Electrical Engineering & Science & Laboratory for Research on the Structure Matter University of Pennsylvania Philadelphia Pa., 19104
- * Electrical Equipment Division MERADCOM Fort Belvoir, Va. 22060

INTERSTITIAL COMPOUND APPROACH

CAN CONVERSION OF GRAPHITE FIBER TO GRAPHITE

OXIDE (FLUORIDE) REDUCE ELECTRICAL CONDUCTIVITY

SIGNIFICANTLY WITHOUT DEGRADING MECHANICAL PROPERTIES?

SYNTHESIS

COMPOSITIONS

STRUCTURES

COVALENT BONDING = HIGH RESISTIVITY

AROMATIC RINGS = HIGH STRENGTH

AND MODULUS

ELECTRICAL RESISTIVITY

GRAPHITE OXIDE SYNTHESIS

BRODIE, HOFFMAN, STAUDENMAIER

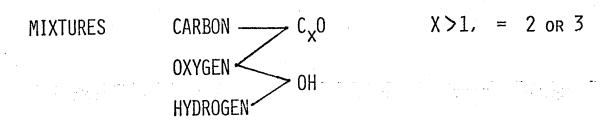
TIME CONSUMING, HAZARDOUS

GRAPHITE +
$$H_2SO_4$$
 + $NANO_3 \\ KMNO_4$ = $GRAPHITE \\ OXIDE$

HUMMERS AND OFFEMAN

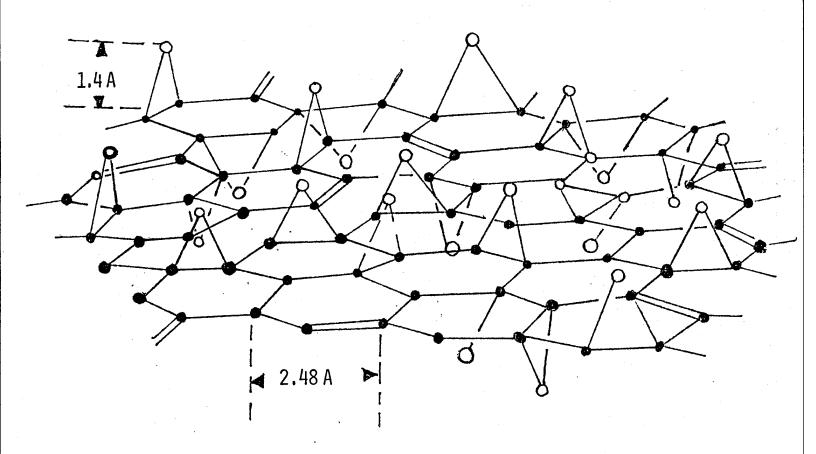
RAPID REACTION - NO HAZARD

GRAPHITE OXIDE COMPOSITIONS



CARBON RATIO	COLOR
16	BLACK
3	GREEN
2	YELLOW

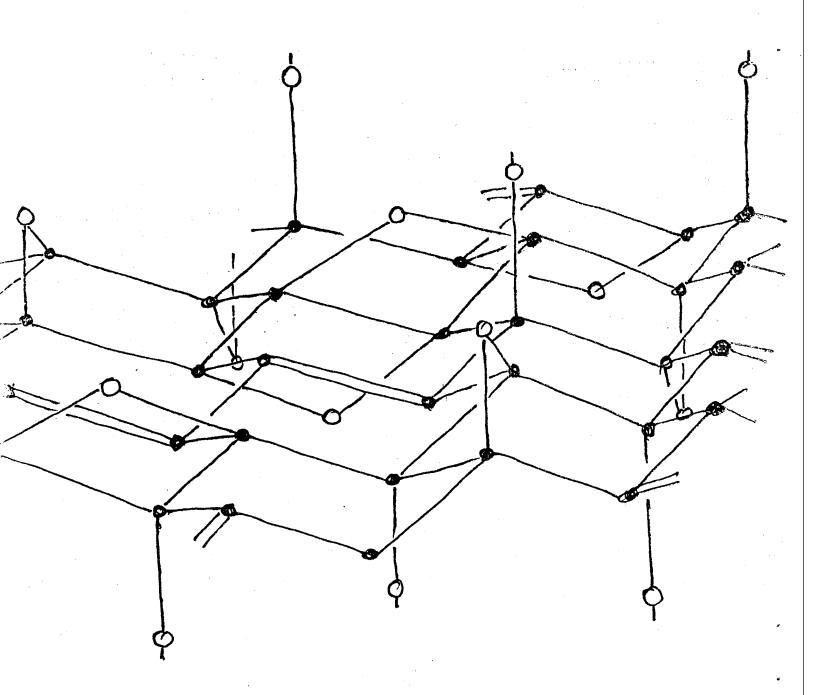
GRAPHITE OXIDE STRUCTURE



- O OXYGEN ATOM
- CARBON ATOM

FROM HOFFMAN, FRENZL, CSALAN

GRAPHITE OXIDE STRUCTURE



- O OXYGEN ATOM
- CARBON ATOM

FROM CLAUSS, PLASS, BOEHM, HOFFMAN

GRAPHITE OXIDE ELECTRICAL RESISTIVITY

CARBON OXYGEN RATIO	RESISTIVITY (DRY) OHM-CM
3.0	10 ⁷
3.5	4,000
4.3	250
7.1	0.4
12	0.2
21	0.05
GRAPHITE .	0.023

SILICON CARBIDE, BORON, AND GLASS COATED GRAPHITE FIBERS

FRANCIS GALASSO
UNITED TECHNOLOGIES RESEARCH CENTER

MARCH 23, 1978

Modulus x10⁶psi

3 Hours

1 Hour

100.0

14.8

39.5

37

51

Hercules HTS

Hercules HMS

⁵ Celanese DG 102

36.1

16.7

57

Thornel 50

Thornel type P

5.3

9

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Fiber	%Loss in	in weight (550°C)	20 ₀ C)
	1 Hour	3 Hours	6 Hours
1 HMS	34.8	77.0	88.6
2 HMS	6.1	20.9	39.4
3 HMS	12.4	27.7	52.0
1 HTS	3.1	17.1	93.9
2 HTS	4.9	21.8	97.8
3 HTS	3.8	13.6	34.3
AS	78.3	. 1	l
T300	71.4	ı	I

56

Graphite Fiber Coating Program

Molten glass

J. Bacon

Colloidal silica

Dip coating

Electrophoretic coating

S. Holmquist

Organo-silicon compounds

Dip and conversion

D. Scola H. Roth and

R. Veltri

and F. Galasso

CVD B

CVD SiC

and F. Galasso R. Veltri



Ø
}
Ø
-
$\boldsymbol{\omega}$
\rightarrow

Sic

B₄C

Tic

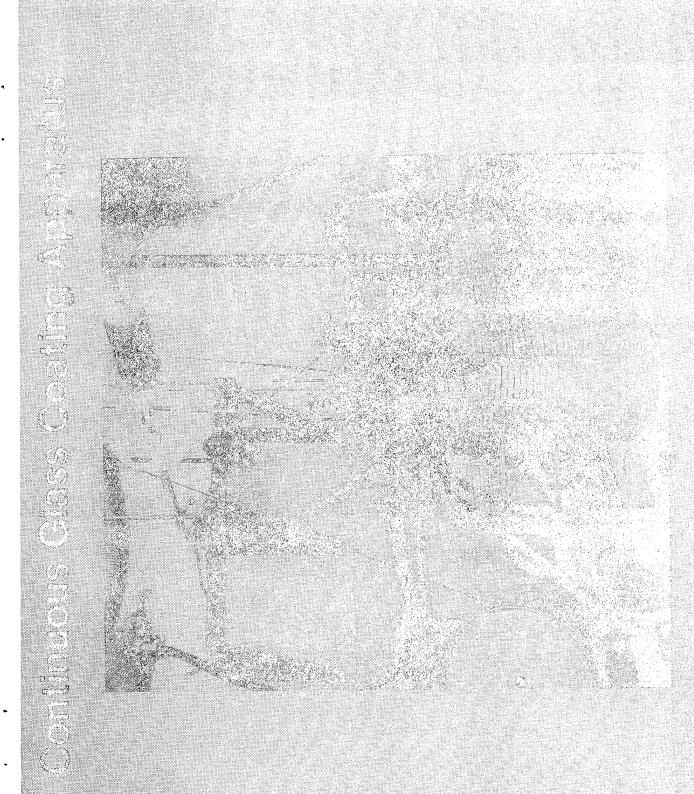
BN

Si₃N₄ SiO₂

Resistivity (ohm-cm)

$$10^{3} - 10^{5}$$

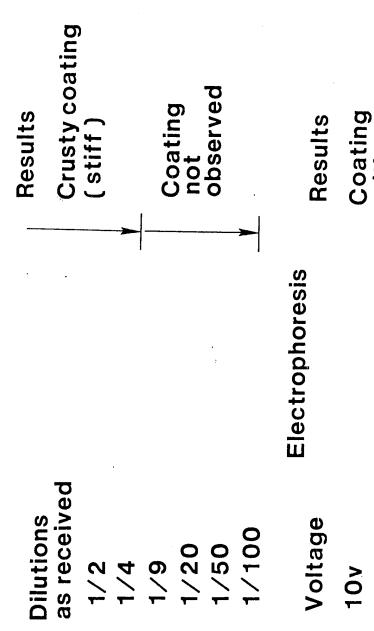
$$5 \times 10^{-1}$$



Colloidal SiO₂

. (30%)

Dip Coating



61

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given off at electrode

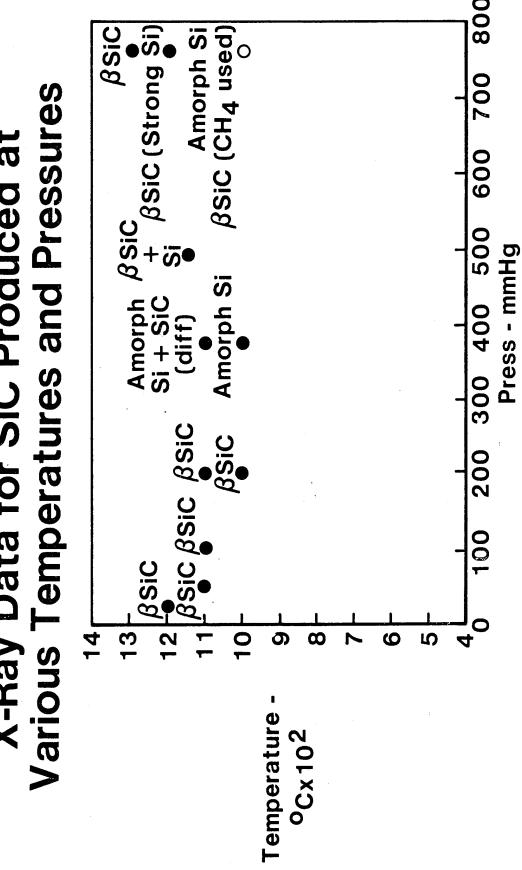
with 02

5 <

Organo-Silicon Coatings and Thermal Conversion

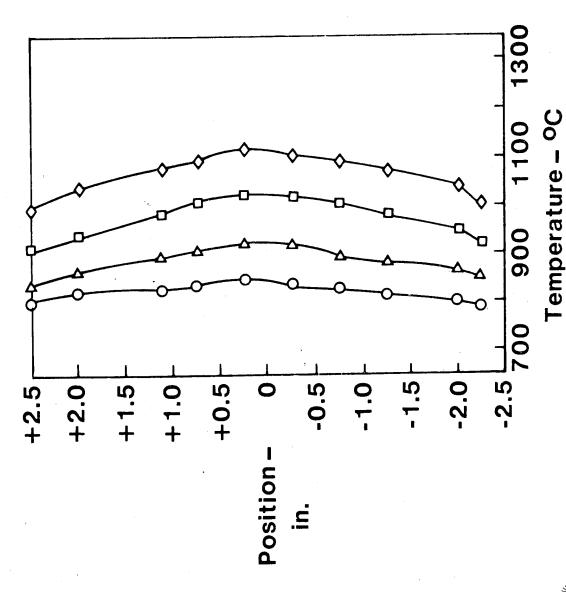
	Material deposited	Number of coats	EDAX analysis Si deposited/ Si background
	CH3-Si-(OC ₂ H ₅) ₃ (methyltriethoxysilane)	ل ک	Trace
•	CH ₂ =CH-Si- O-C-CH ₃) ₃ (Vinyl triacetoxysilane)	- S	230/100
	Silicone resin G.E. SR 355	•	Trace
		Ŋ	1100/100
	Ethyl silicate prepolymer	•	675/100
		S.	2250/100

X-Ray Data for SiC Produced at

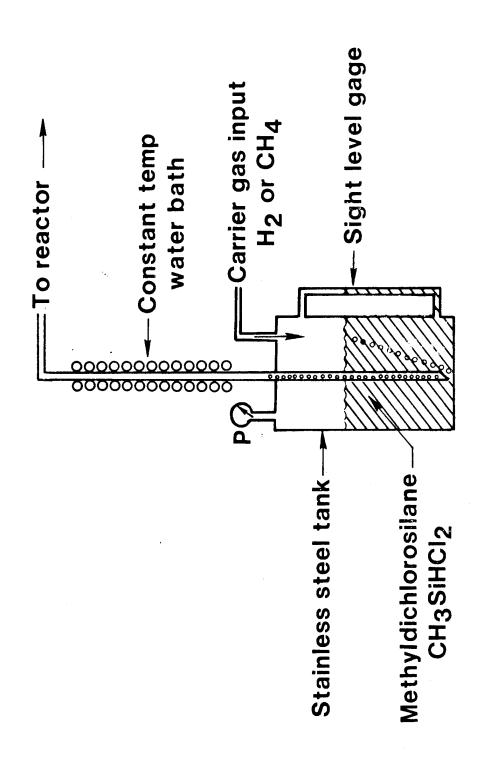


63

Thermal Profile in Reactor Zone for Four Power Levels

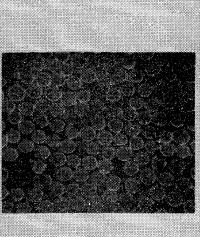


Silane Evaporator

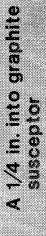




SiC on Graphite Fiber Static Run



B 1 in. into graphite susceptor





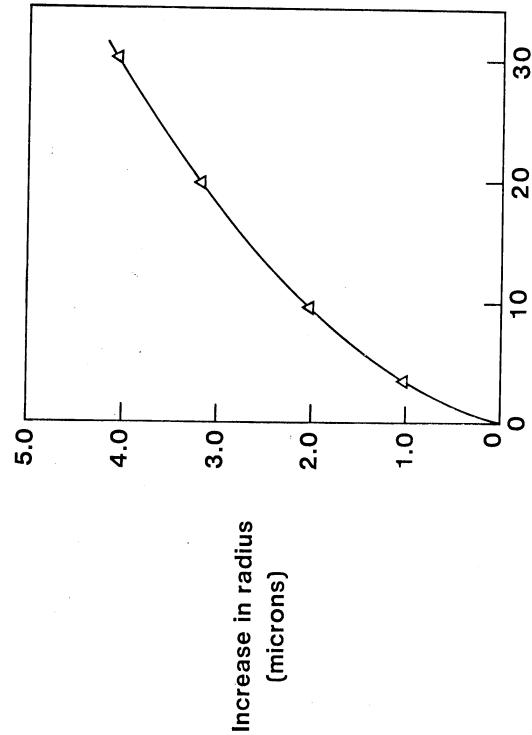
C 1/2 in, over graphite susceptor

Deposition Rate

Temp 1050 °C

Amospheric pressure

Static runs



(microns)

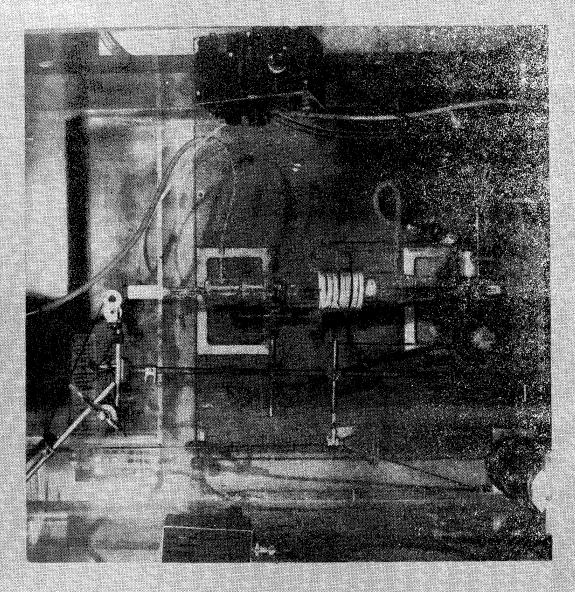
67

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78-02-222-2

Time (minutes)

Chemical Vapor Deposition Apparatus



UNITED TECHNOLOGIES

BORON CARBIDE AND SILICON CARBIDE COATED GRAPHITE FIBERS

RAYMOND J. SUPLINSKAS

AVCO SPECIALTY MATERIALS DIVISION

MARCH 23, 1978

• COATING MATERIALS:

SILICON CARBIDE

BORON CARBIDE

SUBSTRATE

THORNEL 300

• COATING THICKNESS

0.1 MICRON

BULK ELECTRICAL PROPERTIES

• RESISTIVITY

SILICON CARBIDE 100 Ohm-cm

BORON CARBIDE 1 Ohm-cm

GRAPHITE 7 10-3 Ohm-cm

• Sic IS HI-TEMP. SEMICONDUCTOR

BREAKDOWN VOLTAGE - 1100 VOLTS

(1/4" SPECIMEN)

OTHER PROPERTIES

REFRACTORY

DIFFUSION BARRIER

ENHANCED WETTING

OXIDIZED COATINGS

SiO₂ - INSULATOR

B₂0₃ - FUSIBLE

• CVD PROCESS

$$^{4}BC1_3 + CH_4 + 4H_2 \implies B_4C + 12HC1$$

$$4BC1_3 + C + 6H_2$$
 \Rightarrow $B_4C + 12HC1$

RATE CONTROL VS. DIFFUSION CONTROL

CVD PARAMETERS

TEMPERATURE

PLATING GAS COMPOSITION

FLOW GEOMETRY

RESIDENCE TIME

Sketch of CVD Reactor to Produce Carbide Coatings on Graphite Figure 1.

COATING CHARACTERIZATION

SEM

AUGER SPECTROSCOPY

TENSILE TESTS

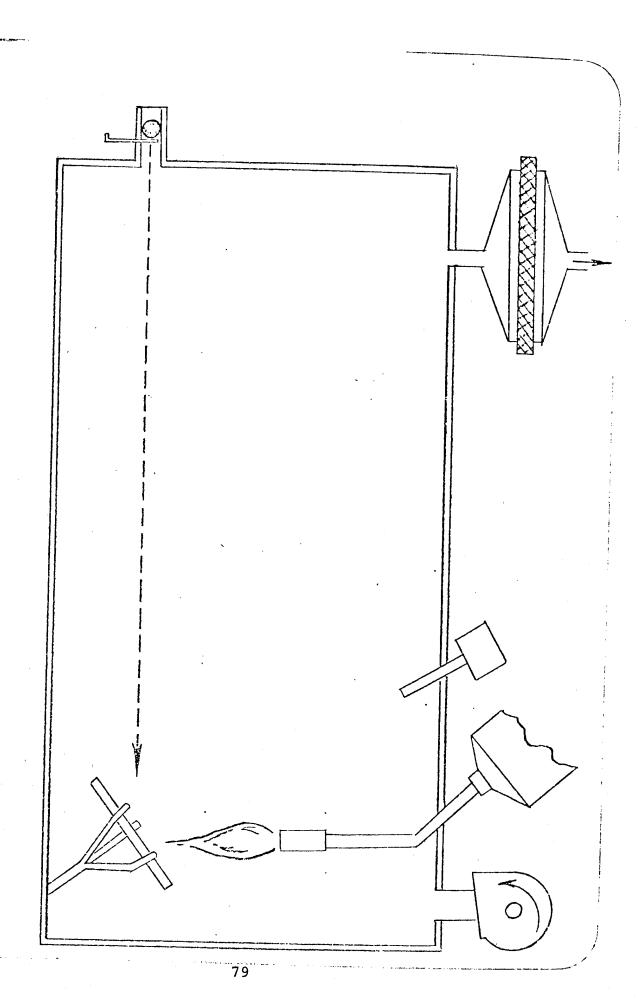
BORON NITRIDE, SILICON CARBIDE AND SILICONE COATED GRAPHITE FIBERS

HERBERT F. VOLK UNION CARBIDE CORPORATION

MARCH 23, 1978

TECHNICAL TASKS

- 1. HIGH RESIDUE SILICON COATINGS.
- 2. BORON NITRIDE COATINGS.
- 3. SILICATE COATINGS.
- 4. SILICONE CARBIDE COATINGS.
- 5. BURN TEST CHAMBER.



COUNTY OF THE STATE OF THE STAT

REVIEW OF NASA-AMES MATERIALS MODIFICATION PROGRAM

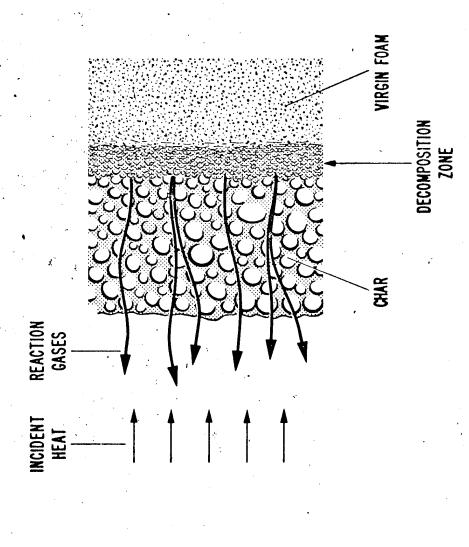
"AN APPROACH TO THE DEVELOPMENT OF FIRE RESISTANT COMPOSITES"

JOHN A. PARKER

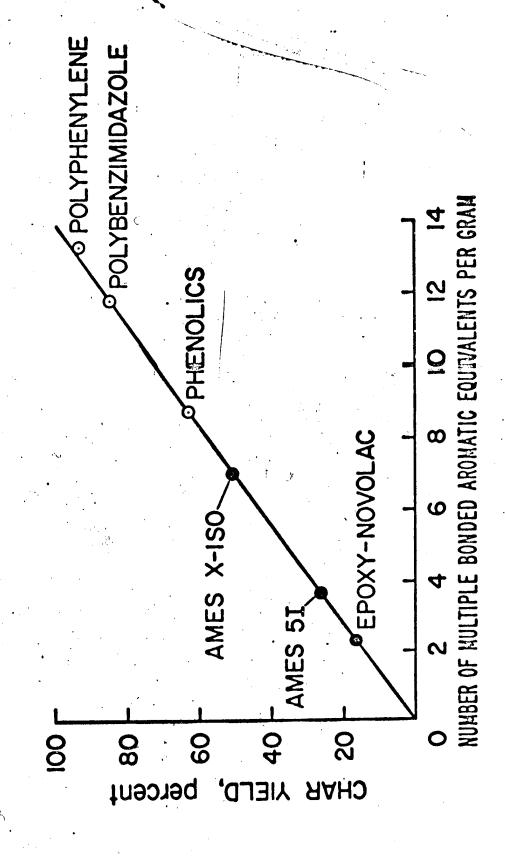
NASA AMES RESEARCH CENTER

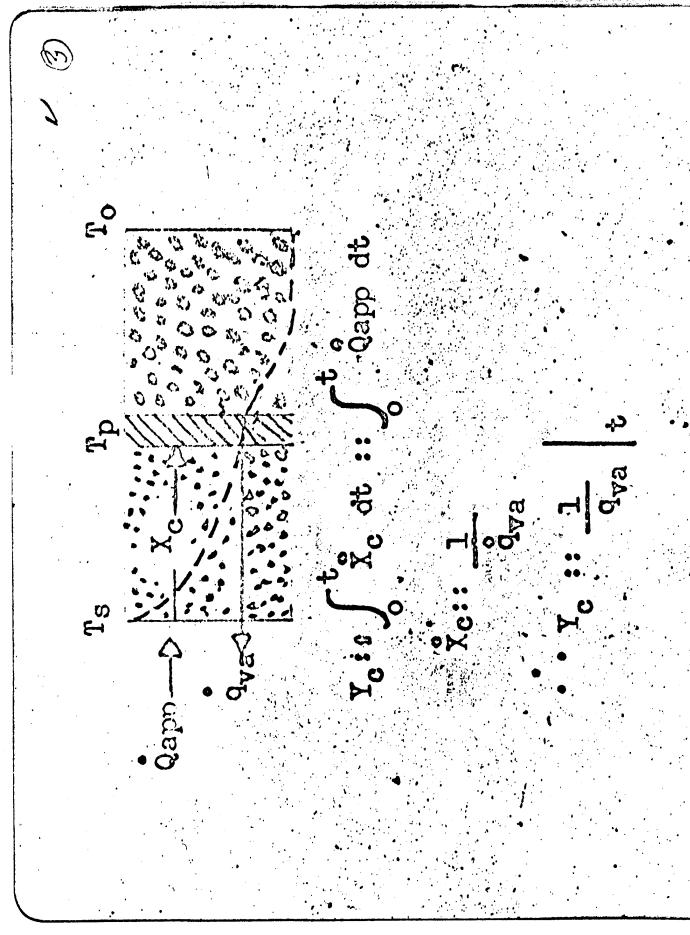
MARCH 23, 1978

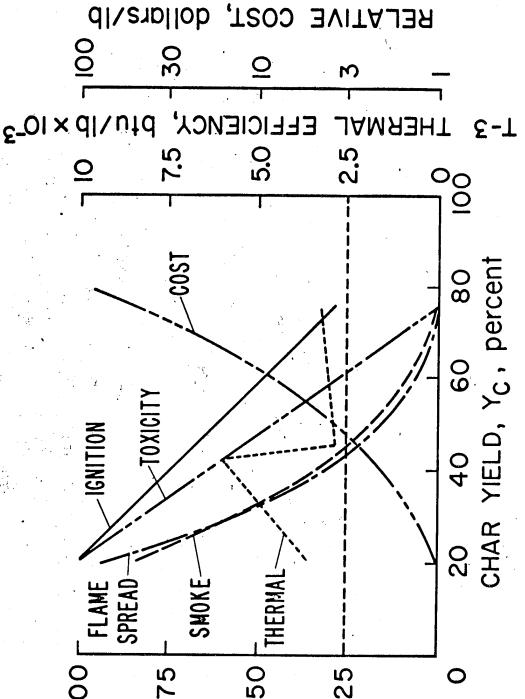
TYPICAL REACTION OF CHAR FORMING FOAMS DUE TO THERMAL LOADS



NAME

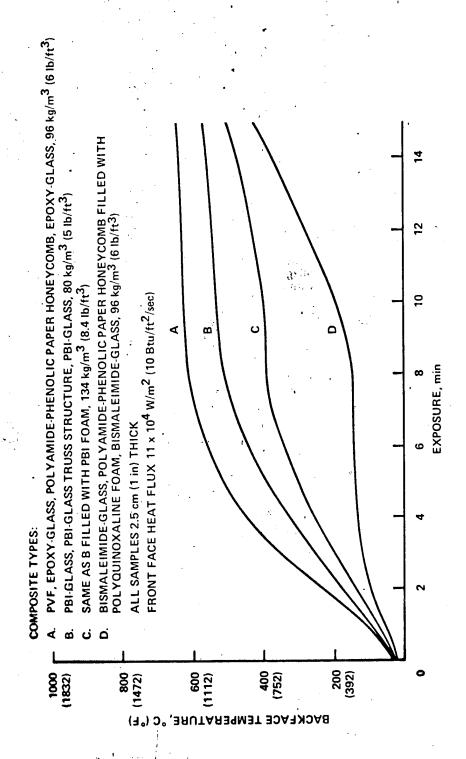






ONE PLY TYPE 181 E GLASS POLYQUINOXALINE FOAM IN 0.005 cm WITH DECORATIVE CHLORENDIC ANHYDRIDE-POLYAMIDE HONEYCOMB POLYCARBONATE FILM, BISMALEIMIDE PREPEG POLYAMIDE ADHESIVE ADVANCED **PHENOLPHTHALEIN** INK ON TOP AND COMPOSITE CONFIGURATION OF AIRCRAFT INTERIOR PANELS **EPOXY ADHESIVE** UNDERNEATH POLYAMIDE PAPER HONEYCOMB -POLYVINYL FLUORIDE, 0.005 cm WITH DECORATIVE INK ON TOP TWO PLIES, TYPE 181, AND METHACRYLATE ADHESIVE UNDERNEATH POLYVINYL FLUORIDE FILM, 0.0025 cm WITH POLYMETHYL TYPE 120 E GLASS EPOXY PREPEG STATE-OF-THE-ART

THERMAL DIFFUSIVITY



COMPARISON OF FLAMMABILITY PROPERTIES OF AIRCRAFT INTERIOR PANELS

• COMPOSITE PROPERTIES	PVF, EPOXY-GLASS POLYAMIDE HONEYCOMB, EPOXY-GLASS	PHENOL POLYCARBONATE, BASMALEIMIDE-GLASS, POLYAMIDE HONEYCOMB FILLED WITH POLYQUINOXALINE FOAM, BISMALEIMIDE-GLASS	
DENSITY (ASTM D 71) FLATWISE TENSILE STRENGTH (ASTM C307),	96 kg/m ³ 0.02-0.05 N/m ²	96 kg/m ³	
24°C FIRE ENDURANCE, NASA AMES T-3 THERMAL TEST FACILITY, TIME (min) TO REACH BACK FACE TEMPERATURE OF 204°C, FRONT FACE HEAT FLUX 11 × 10 ⁴ W/m ²	2	5	
SMOKE DENSITY (NBS), Ds 4 min. SPECIFIC OPTICAL DENSITY		91	
FAR 25.853, VERTICAL TEST METHOD STAND. 191, METHOD 5903	PASSES	PASSES	
 COMPONENT SMOKE DENSITY MAXIMUM SPECIFIC OPTICAL DENSITY (NBS SMOKE CHAMBER) 	POLIVINYL FLUORIDE 7 POLYAMIDE PHENOLIC PAPER 2 EPOXY RESIN 90 GLASS -	PHENOL POLYCARBONATE 5 NOMEX PHENOLIC PAPER 2 BISMALEIMIDE RESIN 9	*
• COMPOSITE MATERIAL BALANCE % BY WEIGHT	POLYVINYL FLUORIDE 7.6 POLYAMIDE PHENOLIC PAPER 20.5 181, 120 GLASS 41.9 EPOXY RESIN 30.0	PHENOL POLYCARBONATE 5.0 POLYAMIDE PHENOLIC PAPER 20.5 181 GLASS 30.0 BISMALEIMIDE RESIN 30.0 POLYQUINOXALINE 14.5	

STATUS OF NEW RESIN MATERIALS DEVELOPMENT

ORJECTIVE

To develop resins which provide enhanced fire resistance, and provide for minimal fiber release in graphite composites subjected to a fire and impact environment.

STATU

- as phenolics and polyimides can, under post-crash fire similation, almost 1. High char yield resins with char yield (800°C, N₂) in excess of 50% such totally eliminate conductive fiber release.
- exhibit poorer fracture toughness than the currently used epoxy resins. Ourrently available aromatic polymers such as phenolics and polyimides
- Currently used epoxy resins are also sensitive to photo-thermal oxidative degradation as well as weathering (humidity) resulting in a resin poor corposite surface.
- Development of new resins which provide both high char yield, fracture toughness and weathering resistance.
- 2. Development of hybrid composites and modified fibers.

SCHOOL

STATUS OF NEW RESIN MATERIALS DEVELOPMENT

APPROACE

Advanced Resin Development and Modifications

- Polystyryl Pyridene (PSP) SNPE (RFP issued)
- . Bismaleimide Technochamie (RFP issued)
- Phenolics Resins obtained from Ciba-Geigy, Fiberite, Narmco
- Other Resins Benzyl Weyerhauser; Epoxy Copolymers New York Polytechnic Institute; HR-600 - Hughes (being procured)
- 2. Curing Agents for Resins.
- New curing agent to reduce voids and to provide optimum fracture-toughness characteristics in new resin-graphite composites
- 3. Hybrid Composites
- Use of metallic coatings to provide oxidation resistance and fire protection
- b. Use of intumescent coating to provide resistance to weathering and fire.
- 4. Fiber Modifications
- Reduce fiber conductivity by heating fibers in various atmospheres (NO etc)
- Evaluate other char forming mechanisms for resin-fiber combinations.

PROGRAM OBJECTIVE: COMPOSITE PRIMARY AIRCRAFT

SPECIFIC OBJECTIVE: COMPOSITE WING STRUCTURES

STRUCTURAL COMPOSITE MATERIALS (743-02-11 RTOP: EVALUATION AND DEVELOPMENT OF ADVANCED

OBJECTIVES: TO SELECT, PREPARE AND EVALUATE RESIN/GRAPHITE FORMULATIONS WHICH ARE MORE FIRE RESISTANT THAN CURRENTLY AVAILABLE STATE OF THE ART

EPOXY/GRAPHITE COMPOSITES.

IS: • EVALUATE ADVANCED RESIN SYSTEMS INCLUDING EPOXIES, NOVOLAC PHENOLICS, POLYIMIDES, PSP AND BISMALEIMIDE.

EVALUATE THERMAL PROTECTION COATINGS.

DETERMINE DEGRADATION OF MECHANICAL PROPERTIES UNDER THERMAL/FIRE LOAD IN STATE OF THE ART AND ADVANCED COMPOSITES. CHARACTERIZE PRODUCTS OF THERMAL/FIRE DEGRADATION

RESIN MATRICES FOR COMPOSITES
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RESIN/CURING AGENT

TYPICAL CHEMICAL STRUCTURE

EPOXY RESIN BASED ON METHYLENE DIANILINE CURED WITH AROMATIC AMINE OR 4.4" DIAMINO DIPHENYL SULPHONE (DDS) CIBA GEIGY MY 720; NARMCO 5208; FIBERITE 1034C

EPOXY RESIN BASED ON DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA) OR 9.9-BIS (4-HYDROXYPHENYL) FLUORENE (DGEBF) OR COPOLYMERS CURED WITH TRIMETHOXYBOROXINE (TMB) OR MDA OR DDS

PHENOLIC NOVOLAC RESIN BASED ON CONDENSATION OF DIMETHOXY-P-XYLENE AND PHENOL CURED WITH HEXAMINE (XYLOK) CIBA GEIGY XYLOK 210

POLYBISMALEIMIDE PREPOLYMER (TECHNOCHEMIE M751)

$$(H_2C-CH-CH_2)_2-N-(0)-CH_2-(0)-N-(CH_2-CH-CH_2)_2 \\ NH_2-(0)-CH_2-(0)-NH_2; NH_2-(0)-SO_2-(0)-NH_2 \\ AMINE$$

$$\begin{array}{c} cH_3 \\ cH_2 - cH - cH_2 - 0 - (0) - c - (0) - 0 - cH_2 - cH - cH_2 \\ 0 \\ cH_3 \\ cH_2 - cH - cH_2 0 - (0) \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \end{array}$$

RESIN CURING AGENT

POLYSTYRYL PYRIDENE RESIN (SNPE.PSP 6030) POLYMETHYLENE POLYPHENYLAMINE (CIBA GEIGY NCNS-12M)

TYPICAL CHEMICAL STRUCTURE

MONOMER A/B, mole/mole: 0.936

$$^{CH_3O}_{+2C_0-C-CH_2}$$
 $^{CH_3O}_{-1}$ $^{OCH_3}_{-1}$ $^{H}_{-1}$ $^{CH_2-C_0-CH_2}_{-1}$

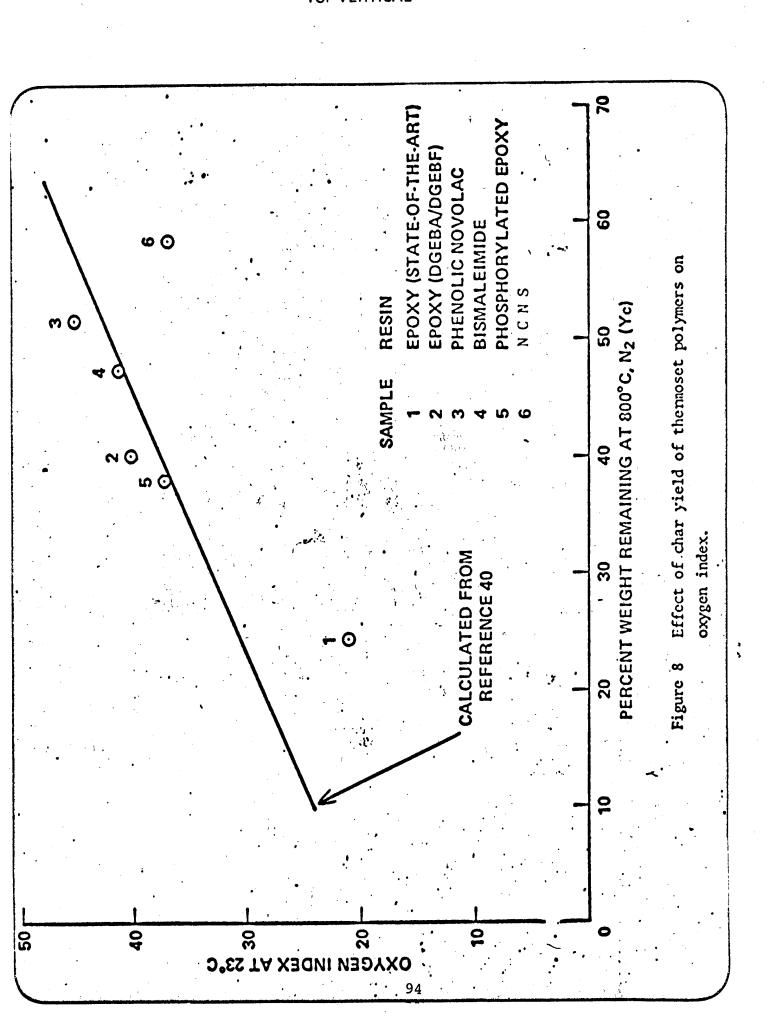
$$\begin{pmatrix} O - C - \left\{ \bigcirc - C - \left\{ \bigcirc - C - \right\} \bigcirc - NH_2 \right\} \\ O H \\ O H$$

PRE-POLYMER + 2n + 2MeOH

BENZYL RESIN (WEYERHAUSER)

TYPES OF COMPOSITE MATRIX RESINS ON THE FIRE SIGNIFICANT THERMOCHEMICAL PROCESS CHARACTERISTICS OF DIFFERENT **ENVIRONMENT**

- THERMOCHEMICAL SCISSION (VAPOR PRODUCTION)
- TEMPERATURE INDUCED CHAIN SCISSION
- a. RANDON CHAIN FRAGMENTATION
- b. SIDE CHAIN ELIMINATION
- RADICAL UNZIPPING MONOMER PRODUCTION
- THERMAL CROSS-LINKING PROCESSES (CHAR **FORMATION**)
- REACTIONS OF CHAIN BEARING CHEMICAI THERMALLY INDUCED BIFUNCTIONAL GROUPS.
- RADICAL SPECIES WHICH COMBINE TO FORM THERMAL CRACKING REACTIONS PRODUCING STABLE POLYCYCLIC AROMATIC MOEITIES.
 - AROMATIZATION INCLUDING CYCLIZATION/ **DEHYDROGENATION.**



CHEMISTRY OF NEW EPOXY RESINS

O-CH2-CH-CH2

नि-देन द्यार ० -

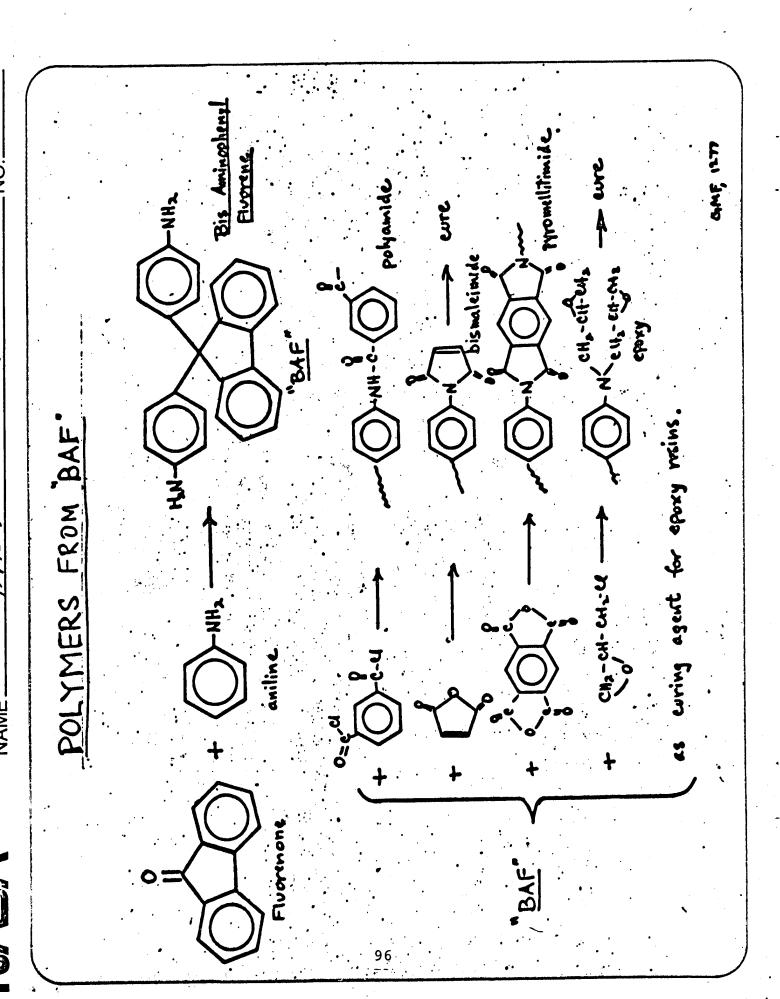
Diglycidyl ether of BPF

DGBPF.

Cored with:

- Aromatic Anhydrides (e.g.: Pyromellitic Dianhydride)
- * Aromatic Amines (e.g.: meta. Phenylene diamine, MDA)
 - · Catalytically: BF3, Trimethoxy boroxine

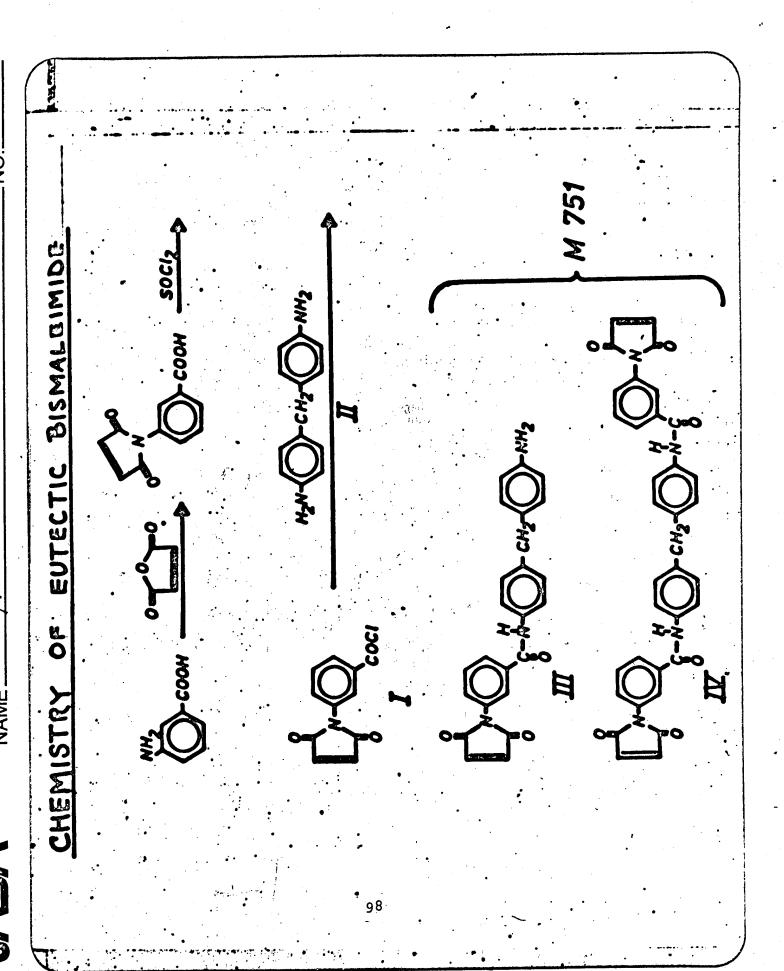
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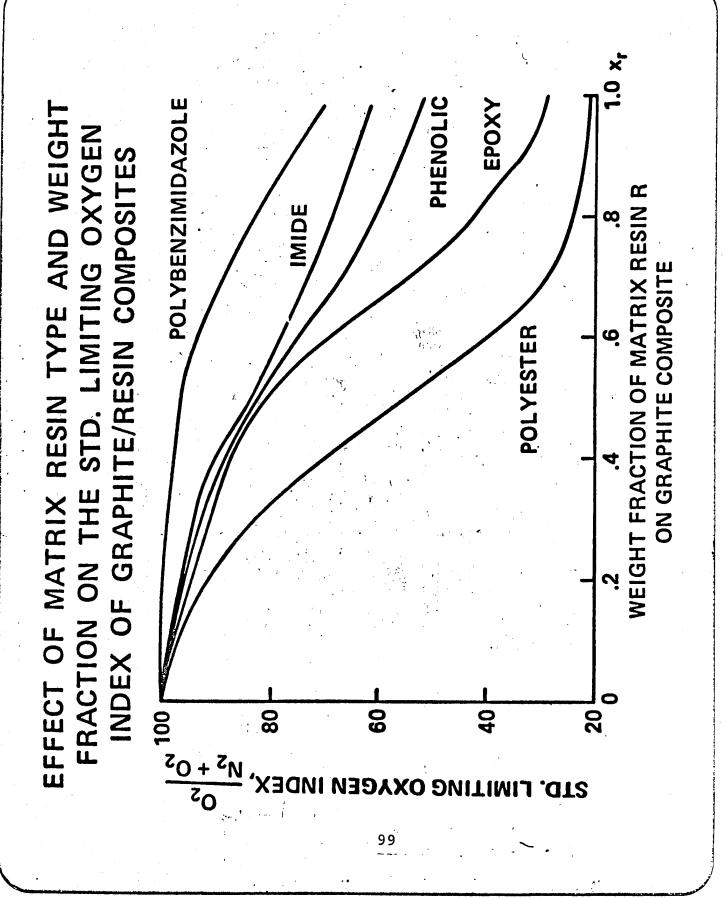


POLY STYRYL PYRIDINE (PSP) POLYMER TEREPHTHAL-CHALDENYOR

FURTHER CONDENSATION

SET FO



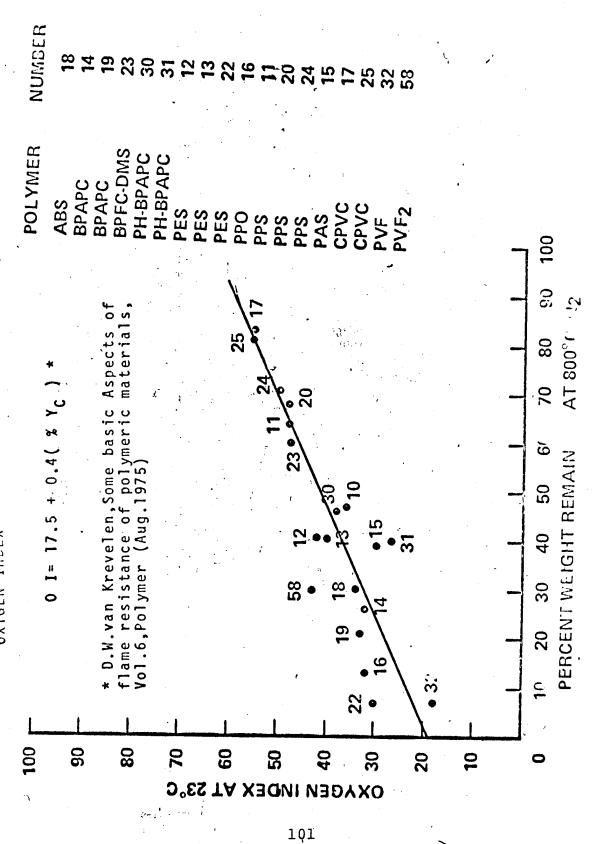


TYPICAL THERMAL AND FLAMMABILITY PROPERTIES OF CANDIDATE RESIN MATRICES FOR GRAPHITE COMPOSITES

NAME.

	•	•		•
RESIN NAME	MY 720.	XYLOK	NCNS	: FURAN
SOURCE	CIBA GEIGY	CIBA GEIGY	CIBA GEIGY	QUAKER
CHEMICAL TYPE	EPOXY	. PHENOLIC NOVOLAC	PHENYLANINE .	FURAN
PROCESSING TEMPERATURE, C	. 120	477	771	. 135
POST CURE, hours/temp °C	4/180	24/250	2/224	2/135
SOLVENT	CURED WITH DDS	MEK	MeCI ₂ 1.	ACETONE
. TGA, Ye 850 C, X, N2.	. 8	. 52	28	69
LOI, NEAT WITH 181 GLASS CLOTH (% RESIN)	21 .23(34)	26 (27)	27 90(29)	(50)09
SMOKE, Ds. 2 min. 2.5 W/cm ² , Ds MAX	80	6 44	89 172	0.8
TOXICITY. ALC50. mg/l	1	. 61	1	i -
HEAT RELEASE OSU, . W.sec/cm2, 5W/cm2	009		÷ 1	
•NEAT RESIN'	••STATE-OF-THE-ART RESIN DDS: DIAMINODIPHENYL SI	IT RESIN , HENYL SULPHONE		
			•	•

EFFECT OF CHAR YIELD OF THERMOPLASTIC POLYHERS ON OXYGEN INDEX



TYPICAL THERMAL AND FLAMMABILTY PROPERTIES OF CANDIDATE RESIN MATRICES FOR GRAPHITE COMPOSITES

IMIDE POLYST 10 10	RESIN NAME	DGEBF/DGEBA.	BENZYL	K601	PSP 6030
## 181 BENZYL BISMALEIMIDE 135 150 182 3/135,3/180 NONE 4/240 ## 181 38 47 ## 181 38 34 ## 26 90(32) 46(30) ## 80 119 480 ## 80 #	SOURCE	POLYTECHNIC	WEYERHAUSER	RHODIA	SNPE/FRANCE
135 150 182 3/135,3/180 NONE 4/240 T TMB WATER. NAMP H 181 38 34 26 90(32) 46(30) 119 480	CHEMICAL TYPE	EPOXY		BISMALEIMIDE	POLYSTYRYL PYRIDIN
3/135, 3/180 NONE WATER. 4/240 H 181 38 34 26 90(32) 8 1 80 119 480	PROCESSING TEMPERATURE, C	135	150	182	250
H 181 38 61 47 47 47 47 47 47 47 47 47 47 47 46(30) 46(30) 46(30) 46(30) 480 480	POST CURE, hours/temp °C	3/135, 3/180	NONE	4/240	NO.
H181 38 26 46(30) 80(32) 8 80 80 119 480	SOLVENT/CATALYST		WATER.	dWN	ANN
H 181 38 26 46(30) 8 10 119 119	TGA, Ye 850 C, N2. X.		, 19		
34 80	LOI, NEAT AND WITH 181 GLASS CLOTH '(% RESIN)	8	34	26 4 6/30)	36
	SMOKE, Dg. 2 min. 2.5 W/cm ² , Dg MAX		ω χ	- Ca	
	TOXICITY, SALCSO, mg/l	1	2		3 8
	HEAT RELEASE OSU, W-tec/cm², SW/cm²	, <u> </u>	1	480	1

DGEBA: DIGLYCIDYL ETHER OF BISPHENOL A TAMB: TRIMETHOXYBOROXINE

TRIMETHOXYBOROXINE N-METHYL PYROLIDONNE

"PRELIMINARY TEST RESULTS OF THE FIBER RELEASE CHARACTERISTICS OF BASELINE GRAPHITE EPOXY COMPOSITES COMPARED WITH NEW CHAR FORMING ANALOGS"

JOHN A. PARKER

NASA-AMES RESEARCH CENTER

MARCH 23, 1978

STATUS OF ENGINEERING AND TESTING OF CC. POSITE MATERIALS

OBJECTIVE

To develop test methods to adequately simulate Crash-Fire (or Fire-Crash) scenarios, to test baseline and modified graphite composite materials, and to determine cost benefit and risk analysis of baseline and modified systems.

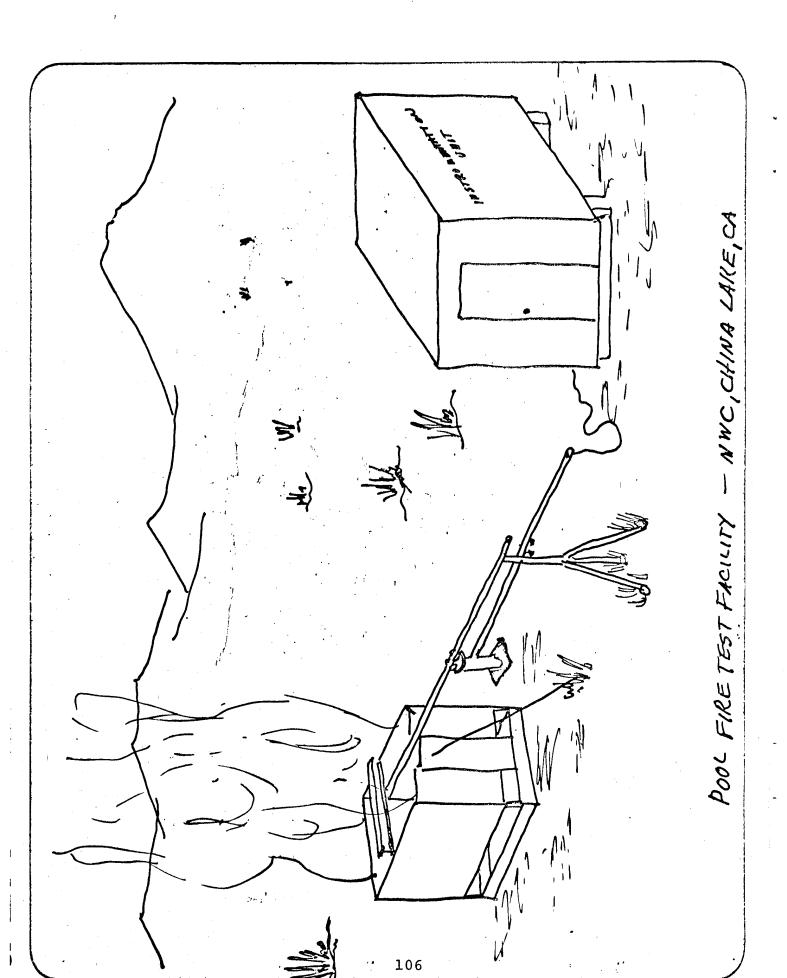
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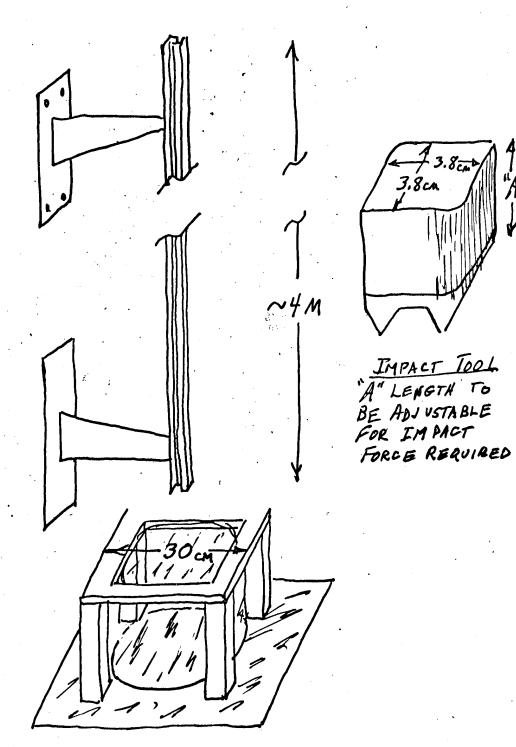
- Laboratory type screening device developed and undergoing initial tests and modifications.
- Larger scale thermal-mechanical test facility being designed based upon postulated limits of typical crash and fire scenarios.
- Proposals sought for fabrication and testing of variant composite systems,
- Proposal being studied for cost benefit analysis model, applicable to variant composite systems.

PPROACE

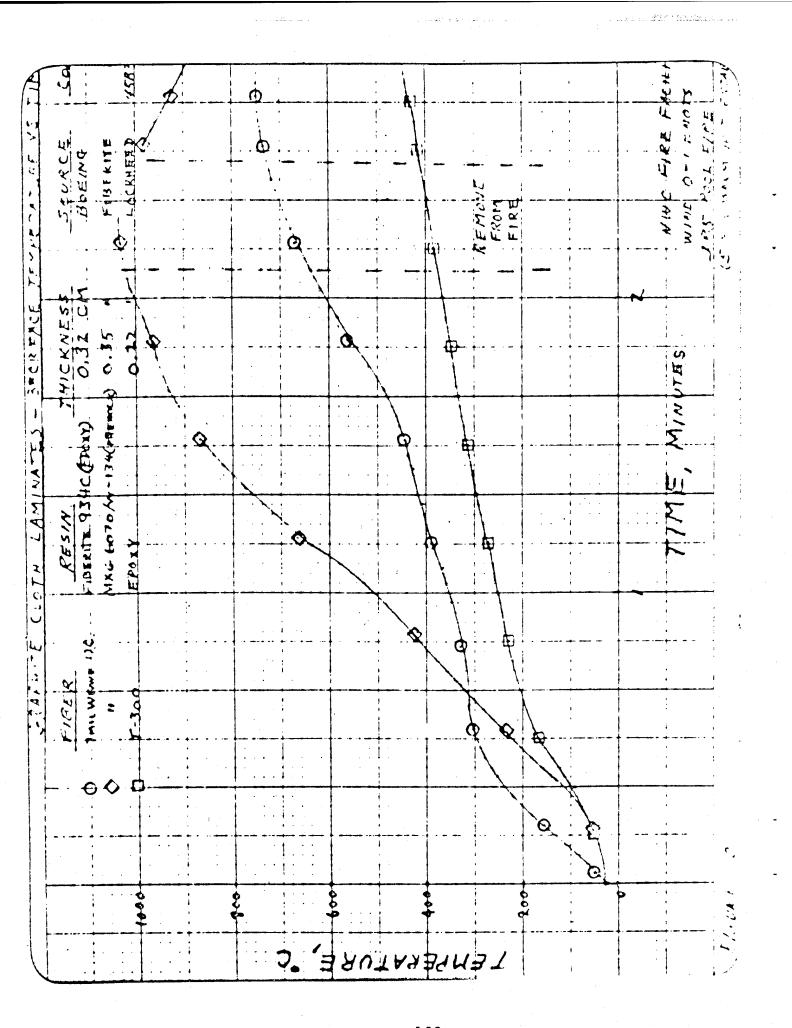
A screening type apparatus will be constructed based upon Garpy Impact testing data include: Breaking energy of baseline and degraded samples: weight loss and fiber release; Characteristics of broken sample, i.e., Critical fiber length, delamination and brittle resin failure; and residual strengthof machine and both direct burning and preheated composite samples. corposite versus temperature.

- heat fluxes, bypass air flows, projectile impact, shock wave interactions, Filtered output to provide for measurement and fiber release classification due to fire, fire and impact, impact and Design and construction of larger scale test facility capable of variant: fire, and fire and shock wave. of fiber release events.
- Baseline and modified composite systems will be tested for mechanical properties, thermochemical properties, environmental properties, and response to thermal-machanical shock.
- Cost benefit and risk analysis models will be developed so that results of tests of modified composites may be used to determine cost benefit mlysis of variant systems.





DROP TESTING FIXTURE, CRPO, AMESRES. CTR.



DEMONSTRATED TECHNOLOGY

CHINA LAKE/AMES TESTS

- POOL FIRE TEST FACILITY/POST-BURN IMPACT
 - BASELINE AND 8 MODIFICATION CONCEPTS

MATERIAL

GR/EP

IBER RELEASE

H16H

MODERATE

MODERATE

GLASS FABRIC ON GR/EP

COATED GR/EP

METAL COATED GR/EP

HIGH

MODERATE

10DERATE MODERATE

NSWC (DAHLGREN) TESTS

GR/IMIDE (HR 600)

GR/PHENOLIC

BURN + EXPLOSION TESTS SHOWED SIGNIFICANT FIBER RELEASE IN GR/PHENOLIC

POLYIMIDE

GLASS FABRIC ON GR/EP

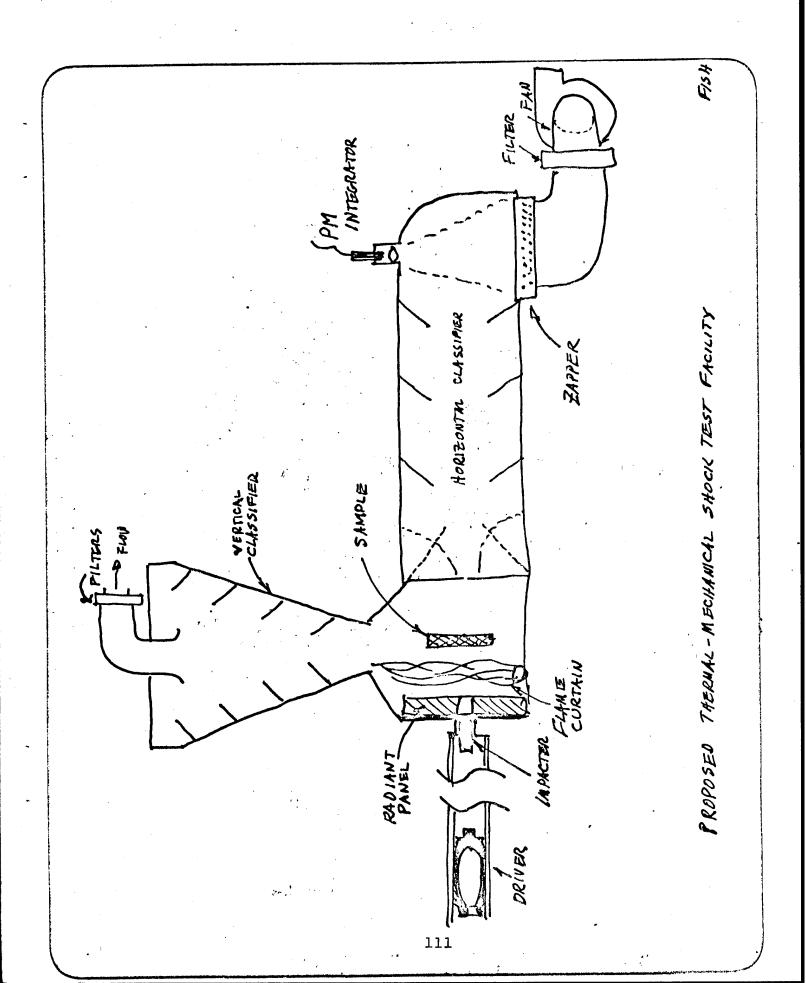
GLASS FILLED PMR

COLLPOSTIE FIRE.

TESTING	
5111101471010	

										1
\	VELOCITY KNOTS	FIRE	Species	IMPUSE DERRE	Perk K Fresure Cshocks Ps1	Presente Velacity m/sec	PRO-SECTIC ARCA	PROSECTION PROJECTIVE DEBRIS FOURTHY	DE BRIS. FYCHTY COOTHING LOCKYNI	Fround Lock Scott
FIRES IN FLIGHT A - EFFECTS OF MR VELOCITY ON DETERIORATION OF BORNING OR BURDT MATERIALS		8-15	YES		i			(٧٠	ARC NWC
PEING CRASH IMPACT	0-30	8-15	sah	> 100 Kts MEXET	TBD	780	SAILL TO	BLUNT TO SHARP	YFS	ARC
FIRES ON GROUND A- DETERIORATION IN POOL FIRE CHAMINIS	0-30	1-15	yes		l		İ		YES	ARC
B - Detertionant of Burning Marchines UNCER INFULSIVE LOADS 1-LOW ORDER SHOCK WAVES! FUEL. AIR EXPLOSIONS; FUEL TAME RUPTURESICE	0-30	1-15	;	At NSec	0010700	02H	LAEGE	BLUMT (SHECK)	YFS	ARC
2 - Low OPSER PUDIORIES RESOLMY FROM FUEL/AIR EXPLOSIONS, ETC.	0-30	1-15		At-ms to secs	180	400	MED	Brewr +• Sykop	45	486
3- Higher order Shoek whies dependent order order	0-30	1-15		Atoms	1 B0	1000 403000	SMALL	SIMP	U.	NWC
TEST DEVICE DESIRAD CAPABILITIES FOR MOST GROBAL USASE.	0 7 0	51-0	YES		55/	0-500	7917	VARY	V. 23 27	

110



STATUS OF MATERIALS MODIFICATION

PROGRAM IN THE CHEMICAL RESEARCH PROJECTS OFFICE

Ames Research Center - Feb. 24, 1978

Most probable conclusions (current opinion) concerning the fiber release threat from involvement of graphite epoxy resin systems in accidental commercial aircraft fires:

POSITIVE RESULTS

- impact energy and sequence is probably not related to real postcrash commercial The fire dynamics and thermal-mechanical impact sequencing used to make initial threat assessment relative to (I) are probably invalid. The fire chemistry, aircraft fires.
- only be required in certain highly crash fire vulnerable areas of domestic aircraft. Graphite structural composties with exceptional fire resistance and integrity may
- accompdate the normal aircraft crash fire without loss of fibers and can also High char yield resin binders (matrix resins) with anaerobic char yields of greater that 60% when used in structural graphite composites can completely provide long time retention of structural integrity in in-flight fires.
- resin systems may significantly reduce the threat without compromising manhanteal reduction of fiber conductivity to a degree that when combined with char founing Minor modifications of currently available graphite fiber systems may provide properties.

STATUS OF MATERIALS MODIFICATION PROGRAM

Problematic Conclusions and Areas Requiring Intensive Effort

- Graphite epoxy structural composites may have an additional fiber release problem due to combined thermal and photo-oxidation environmental effect. Various coatings may resolve this in the short term.
- cost problems. Significant improvements in fracture toughness and impact strengths will have to be made before these resins can be safely used in The use of high char yield resin systems may create minor processing and structural applications.
- The fiber release problem is primarily a polymer flammability and mechanical stability problem.
- composites is confused by the lack of significant connection among crash fire The effect of risk assessment on overall cost benefits for using graphite scenario, crash-impact fire dynamics, crash fire fiber release and test simulation.

STATUS OF CONTRACT AND INTERFACE DEVELOPMENT WITH INDUSTRY AND UNIVERSITY ELEMENTS - Feb. 24, 1978

INDUSTRIAL INTERFACE

A. Materials and Process

I. Resins

- free composites from HR-600 polyimides cured with 1,2 poly addition acetylenic Hughes Aerospace Group, Culver city, CA (Dr. N. Bilow) High char yield, void termination. Briefing conducted. Obtained and tested composite samples. (Proposal being submitted)
- Hitco, Gardena, CA (Dr. George Lee) Prepreg and composite fabrication from new Supplied state-of-the-art test specimens. Investigation of high temperature interface coatings. phenolic and benzyl resin systems.

(Proposal being submitted)

- bismaleimide, epoxy resin systems based on fluorenone bisphenol derivatives and Composites Horizons, Ontario, CA (Dr. Ira Petker) Processability and initial physical properties screening on new experimental resins - i.e., hot melt (Proposal being submitted)
- Technochemie GWEM, Heidliberg, West Germany (Dr. H. Stenzenberger) Davelege at of graphite - bismaleimide prepregs and composites based on hot malt

bismaleimide resins. (Contract being negotiated)

SNPE, Paris, France (Dr. B. Melassine) Development of polystyryl pyridene resin (PSP 6030) for application to graphite composites (Contract being negotiated)

2. Fibers

- coatings with increased resistivity without significantly affecting composite Union Carbide, Parma, Ohio (Dr. B. H. Eckstein) Application of carbon fiber performance or fabrication cost. (Discussions being held for a proposal)
- graphite fibers by coating or "doping" with high resistance silica, glan, boron, Cellanese Research Division, Summit, New Jersey (Dr. J. Leal) Modification of metal carbides (Discussions for proposal; presentation to be made)

I. University Interface

of resins on the thermochanical and flammability properties of epoxy and other advanced resins University of Utah, Salt Lake City, Utah (Dr. A. Sosin) Study of the effects of optimum cure (Contract in final stages of negotiation).

Eciytechnic Institute of New York, Brooklyn, New York (Dr. E. Pearce) Synthesis of modified epoxy resins and copolymers. (Grant proposal being discussed).

ENCHAERING TESTING AND NODELING

Econ, Inc., San Jose, California - Modeling and cost benefit analysis of various (Contract being negotiated) composites

Douglas Aircraft Company, Long Beach, California - Environmental testing of (Discussions only). composite structures Lockheed Aircraft Company, Burbank, California - Aircraft fire testing of composite (Discussions only) structures

San Jose State University, San Jose, California - Design and computation of mechanical test devices for composites (Continuation of existing Grant) University of California, Berkeley, California - Design and construction of crash fire test facility for graphite composites. REVIEW OF NASA LEWIS MATERIALS MODIFICATION PROGRAMS TITO T. SERAFINI NASA-LEWIS 3-23-78

MASA-LEWIS MATERIAL

MODIFICATION PROGRAM

OBJECTIVE:

OF POLYMER MATRIX/GRAPHITE FIBER COMPOSITES WHILE ELIMINATING THE HAZARD TO UN-PROTECTED ELECTRICAL EQUIPMENT CAUSED BY GRAPHITE FIBER RELEASE IN FIRE RELATED TO DEVELOP COMPOSITE MATERIALS WHICH HAVE THE DESIGNABLE HIGH PERFORMANCE PROPERTIES ACCIDENTS.

MAJOR THRUSTS:

DEVELOPMENT OF NEW AND/OR IMPROVED MATRIX RESINS

IDENTIFICATION OF ALTERNATE FIBER MATERIALS

CONSTITUENT MATERIALS WHEN SUBJECTED TO SEVERE OXIDATIVE CONDITIONS. DEVELOPMENT OF HYBRID COMPOSITES WHICH EXHIBIT IMPROVED RETENTION OF

I FR

TITLE: SYNTHESIS OF IMPROVED PHENOLIC RESINS

TO SYNTHESIZE PROCESSABLE PHENOLIC RESINS FOR USE AS MATRIX RESINS OBJECTIVE:

IN HIGH PERFORMANCE FIBER REINFORCED COMPOSITES.

PERIOD OF PERFOMRANCE: 12 MONTH

STATUS: PROPOSALS DUE MARCH 26, 1973

TITLE: SYNTHESIS OF IMPROVED POLYESTER RESINS

TO SYNTHESIZE POLYESTER RESINS WITH IMPROVED CHAR FORMING OBJECT IVE:

CHARACTERISTICS,

PERIOD OF PERFORMANCE: 12 MONTH

STATUS: PROPOSALS DUE APPLIL 6, 1973

TITLE: SILICONE COPOLYMERS FOR COMPOSITE MATRIX APPLICATIONS

TO SYNTHESIZE COPOLYMERS INCORPORATING SILICONE RESINS OBJECTIVE:

WITH ENGINEERING RESINS TO PROVIDE MATRIX MATERIALS

FOR ADVANCED FIBER COMPOSITES,

PERIOD OF PERFORMANCE: 12 MONTH

STATUS: PROPOSALS DUE APRIL 3, 1978

TITLE: SURVEY OF INORGANIC POLYMERS

TO SURVEY THE LITERATURE PERTAINING TO INORGANIC POLYMERS OBJECTIVE:

AND TO IDENTIFY POLYMERS WITH HIGH POTENTIAL FOR USE

AS MATRIX RESINS IN ADVANCED COMPOSITES.

PERIOD OF PERFORMANCE: 6 MONTH

STATUS: PROPOSALS ARE BEING EVALUATED

ITLE: ULTRA-HIGH MODULUS ORGANIC FIBERS

TO DEMONSTRATE THE LABORATORY SCALE PRODUCTION OF ORGANIC FIBERS OBJECTIVE:

HAVING TENSILE STRENGTHS AND MODULI IN THE RANGES OF 400 TO

450 KSI AND 25 TO 30 X 10^6 PSI, RESPECTIVELY.

PERIOD OF PERFORMANCE: 12 MONTH

STATUS: PROPOSALS DUE MARCH 29, 1978

TITLE: HYBRIDIZED POLYMER MATRIX COMPOSITES

TO CONCEIVE, FABRICATE AND EVALUATE HYBRIDIZED POLYMER MATRIX OBJECTIVE; COMPOSITES WHICH EXHIBIT IMPROVED CONSTITUENT MATERIALS'

RETENTION CHARACTERISTICS WHEN SUBJECTED TO SEVERE OXIDA-

TIVE ENVIRONMENTS.

PERIOD OF PERFORMANCE: 12 MONTH

STATUS: PROPOSALS DUE APRIL 3, 1978

PHTHALEIN PWR POLYIMIDES

TO MINIMIZE THE LOSS OF CONSTITUENT MATERIALS FROM GRAPHITE OBJECTIVE:

FIBER/ PMR POLYIMIDE COMPOSITES SUBJECTED TO COMBUSTIVE

ENVIRONMENTS BY INCREASING THE CHAR YIELD OF THE MATRIX

ESIN.

APPROACH: PREPARE PHTHALEIN MODIFIED PMR POLYIMIDES

STATUS: NEW TASK, MONOMERS SYNTHESIS IN PROGRESS

PRINCIPAL INVESTIGATOR: W. ALSTON

LEVEL OF EFFORT: 0.2 MY

IMPROVED PHENOLIC RESINS

TO SYNTHESIZE PHENOLIC RESINS HAVING IMPROVED PROCESSING OBJECT IVE:

CHARACTERISTICS

SYNTHESIS OF LOW MOLECULER WEIGHT PHENOLIC RESIN PRECURSORS APPROACH:

HAVING PENDENT OLEFINIC GROUPS CAPABLE OF ADDITION -

TYPE POLYMERIZATION

STATUS: NEW TASK - MATERIALS SELECTION IN PROGRESS

PRINCIPAL INVESTIGATOR: PETER DELVIGS

LEVEL OF EFFORT: 0.2 MAN-YEAR

CHAR FORMING FPOXY MATRIX RESINS

TO MINIMIZE THE LOSS OF CONSTITUENT MATERIALS FROM GRAPHITE OBJECTIVE:

FIBER/ EPOXY COMPOSITES SUBJECTED TO COMBUSTIVE ENVIRONMENTS BY INCREASING THE CHAR YILED OF THE MATRIX RESIN.

INVESTIGATE THE FOLLOWING FOR MODIFICATION OF EPOXY RESINS AND CURING AGENTS: APPROACHES:

PHTHALEIN GROUPS

PHENOLIC RESINS (NOVOLACS)

PHOSPHATES AND PHOSPHATE ESTERS

D. IMIDES

STATUS: NEW TASK

PRINCIPAL INVESTIGATORS: W. ALSTON AND P. DELVIGS

LEVEL OF EFFORT: 0.4 MY

IMPROVED POLYESTERS

TO SYNTHESIZE POLYESTER RESINS HAVING IMPROVED HEAT RESISTANCE AND CHAR - FORMING CAPABILITY OBJECTIVE:

SYNTHESIS OF NEW VINYL - TYPE CURING AGENTS CONTAIN-ING IMIDE OR QUINOXALINE STRUCTURES APPROACH:

STATUS: NEW TASK - MATERIALS SELECTION AND SYNTHESIS HAVE

BEEN INITIATED

PRINCIPAL INVESTIGATOR: PETER DELVIGS

0.3 MAN-YEAR

LEVEL OF EFFORT:

128

CHARACTERIZATION OF RESINS FOR GRAPHITE FIBER CONTAINMENT

OBJECTIVE: TO DETERMINE THE MODE AND EXTENT OF DEGRADATION OF CANDIDATE RESINS AND COMPOSITES.

THE THERMAL AND OXIDATIVE DEGRADATION PRODUCTS EMITTED TECHNICAL APPROACH:

FROM CANDIDATE RESINS AND COMPOSITES ARE BEING

INVESTIGATED USING PYROLYSIS-GC TECHNIQUES, TH

AMOUNT OF CHAR RESIDUE ALSO WILL BE MEASURED.

PROCEDURES ARE BEING ESTABLISHED. PRELIMINARY RESULTS PROGRAM STATUS:

ON PMR-15 RESINS HAVE BEEN OBTAINED.

PRINCIPAL INVESTIGATOR: R. E. GLUYAS

LEVEL OF EFFORT: 0.3 MY

CHARACTERIZATION OF CHAR RESIDUES

RESIDUES FROM CANDIDATE RESINS AND COMPOSITES. OBJECTIVE: TO DETERMINE THE STRUCTURE AND COMPOSITION OF CHAR

TECHNICAL APPROACH: OPTICAL AND SCANNING ELECTRON MICROSCOPY WILL BE USED

TO CHARACTERIZE CHAR RESIDUES. ALSO, THE ELEMENTAL

COMPOSITION OF THE CHAR RESIDUES WILL BE ANALYZED.

PROGRAM STATUS: WORK BEING STARTED

PRINCIPAL INVESTIGATOR: R. E. GLUYAS

LEVEL OF EFFORT: 0.1 MY

THERMAL ANALYSIS OF IMPROVED MATRIX RESINS

THERMAL-OXIDATIVE STABILITY OF ORGANIC AND IN-OBJECTIVE: TO DETERMINE THE REACTIVITY, THERMAL STABILITY AND ORGANIC POLYMER MATERIALS.

CHARACTERIZE THE THERMAL RESPONSE OF SELECTED POLYMER MATRIX MATERIALS. INITIAL ANALYSES WILL BE DIRECTED THERMAL ANALYSES (DSC, DTA, TGA) WILL BE CONDUCTED TO APPROACH:

TOWARD:

(A) CHARACTERIZATION OF RESIN CURE.

(B) CHARACTERIZATION OF THERMAL DEGRADATION. (C) CHARACTERIZATION OF THERMAL-OXIDATIVE STABILITY

(C) CHARACTERIZATION OF THERMAL-UXIDATIVE STABILITY AND TO DEVELOP CRITERIA FOR RELATIVE STABILITY AND TO CORRELATE THESE ANALYTICAL TEST CRITERIA WITH LARGER SCALE COMBUSTION TESTS.

TECHNICAL CAPABILITY ESTABLISHED; INSTRUMENTAL CAPABILITY TO BE EXPANDED; MATERIALS SELECTION IN PROGRESS. STATUS:

PRINCIPAL INVESTIGATOR: RICHARD W. LAUVER

LEVEL OF EFFORT: 0.2 MY

SPECTRAL CHARACTERIZATION OF HIGH PERFORMANCE MATRIX RESINS

OBJECTIVE: TO CHEMICALLY CHARACTERIZE SOLUBLE MONOMERS, PRECURSORS, CRITICAL TO THE PROCESSABILITY AND PERFORMANCE OF MATERIALS TO ELUCIDATE REACTIONS AND MECHANISMS AND OLIGOMERS OF ORGANIC AND INORGANIC POLYMER THE MATERIALS.

MATRIX MATERIALS, INITIAL ANALYSES WILL BE DIRECTED INSTRUMENTAL ANALYSES (NMR, IR, ESCA) WILL BE CONDUCTED TO CHARACTERIZE THE CHEMISTRY OF SELECTED POLYMER FOWARD: APPROACH:

PURITY AND REACTIVITY OF MONOMERS AND PRECURSORS. 8

DENTIFICATION OF REACTION MECHANISMS AND SEQUENCE DISTRIBUTIONS IN SELECTED POLYMERS AND COPOLYMERS. (B)

(C) IDENTIFICATION OF SOLUBLE OXIDATION PRODUCTS OF POLYMERS AND MODEL COMPOUNDS.

FACILITY CURRENTLY BEING INSTALLED; MATERIALS SELECTION STATUS: TECHNICAL CAPABILITY ESTABLISHED; NEW HETERONUCLEAR NMR IN PROGRESS.

PRINCIPAL INVESTIGATOR: RICHARD W. LAUVER

LEVEL OF EFFORT: 0.2 MY

LERC

STRUCTURAL CHARACTERIZATION OF RESINS AND COMPOSITES

COMPOSITE COATINGS BY FOURIER TRANSFORM INFRARED TO CHARACTERIZE NEW RESIN SYSTEMS, COMPOSITES AND SPECTROSCOPY. OBJECTIVE:

TION ABOUT IMPROVED RESIN SYSTEMS, HYBRIDIZED POLYMER BE USED TO OBTAIN MOLECULAR STRUCTURAL INFORMA-FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY WILL MATRICES, AND COMPOSITE COATINGS. APPROACH:

KATHERINE E, REED PRINCIPAL INVESTIGATOR:

0.2 MY LEVEL OF EFFORT: LERC

DYNAMIC MECHANICAL TESTING OF RESINS AND COMPOSITES

TO EXAMINE THE DYNAMIC MECHANICAL PROPERTIES OF HYBRID COMPOSITES AND RESIN SYSTEMS. OBJECTIVE:

DYNAMIC MECHANICAL ANALYSIS (DMA) WILL BE USED TO APPROACH:

EXAMINE THE EFFECT OF MIXED RESIN AND OTHER HYBRID

SYSTEMS ON THE TEMPERATURE-DEPENDENT FREQUENCY

AND DAMPING CHARACTERISTICS OF THE COMPOSITE.

PRINCIPAL INVESTIGATOR: KATHERINE E. REED

LEVEL OF EFFORT: 0.1 MY

HYBRIDIZED POLYMER MATRIX COMPOSITES

TO FABRICATE AND EVALUATE HYBRIDIZED POLYMER MATRIX OBJECTIVE:

COMPOSITES WHICH EXHIBIT IMPROVED CONSTITUENT

MATERIALS RETENTION CHARACTERISTICS WHEN SUBJECTED

TO SEVERE OXIDATIVE ENVIRONMENTS.

FABRICATE AND CHARACTERIZE PMR POLYIMIDE AND EPOXY APPROACH:

RESIN MATRIX COMPOSITES OF KEVLAR/SILICON CARBIDE,

KEVLAR/ALUMINA AND KEVLAR/GRAPHITE FIBERS,

PRINCIPAL INVESTIGATORS: M. P.

M. P. HANSON K. J. BOWLES

LEVEL OF EFFORT: 1.1 MY

LERC

I FR

POLYMER ADDITIVES FOR FIBER CONTAINMENT

TO INVESTIGATE POLYMER BLENDS AND INORGANIC FILLERS FOR OBJECTIVE:

MINIMIZING LOSS OF CONSTITUENT MATERIALS FROM

GRAPHITE FIBER COMPOSITES SUBJECTED TO COMBUSTION,

PMR POLYIMIDE, EPOXY AND POLYESTER RESINS BLENDED WITH APPROACH:

VARIOUS COMMERCIALLY AVAILABLE SILICONE COMPOUNDS

OR INORGANIC FILLERS WILL BE INVESTIGATED FOR:

I. COMPATIBILITY

. CHAR FORMATION

PROCESSABILITY

I. FIBER CONTAINMENT

5. COMPOSITE PROPERTIES

STATUS: WORK INITIATED

PRINCIPAL INVESTIGATOR: R. D. VANNUCCI

LEVEL OF EFFORT: 0.5 MY

PRELIMINARY BURNING RIG EXHAUST WITH ----FILTER == CHAMBER CAP PYREX CHAMBER SAMPLE AND BURNER HOLDER THERMOCOUPLES METHANE-AIR RESIDUE CUP === DIAMETER: 7 INCHES IMPACTOR === LENGTH: 36 INCHES

BURNER. RIG FEATURES

- . SAMPLE VISIBILITY
- PARTICULATE COLLECTION
- HEPA FILTER & RESIDUE CUP
 - SMOOTH INNER SURFACES
 - EASY DISASSEMBLY
- LARGE AIR FLOW
-) DIRECT PARTICULATE MATTER TOWARD FILTER
 - B) COOL FLAME PRODUCTS
- 4. INSTRUMENTATION
- GAS FLOW METERING
- FLAME AND SAMPLE TEMPERATURE MEASUREMENT
 -) CHAMBER AIR FLOW MEASUREMENT
 - D) FILTER PRESSURE DROP
- 5. IMPACTOR
- () SPRING DRIVEN PISTON
-) GAS DRIVEN PISTON
- C) POSITIONED BELOW SAMPLE
- 6. HEAT FLOW UP TO 20 BTU FT² SEC

SUMMARY OF LEWIS IN-HOUSE PROGRAMS

LEVEL OF EFFORT IN FY 79 (MY)

1.1	T. T.	1.6	3.8
RESIN SYNTHESIS	MAIEKIALS CHAKACIEKIZALIUN	HYBRIDIZED COMPOSITES	TOTAL

FIBER RELEASE TESTING FACILITIES AND RESULTS

V. L. BELL MARCH 23, 1978

FIBER RELEASE TEST FACILITIES

PROBLEM:

HOW TO DETERMINE AMOUNTS AND TYPES OF GRAPHITE FIBERS FROM CIVILIAN AIRCRAFT CRASH/FIRE SITUATIONS ?

EXPERIENCE:

NO KNOWN CRASHES OF CIVILIAN AIRCRAFT WITH GRAPHITE COMPOSITE PARTS. SEVERAL CRASHES OF MILITARY AIRCRAFT RELEASED FREE GRAPHITE FIBERS.

TEST LIMITATIONS:

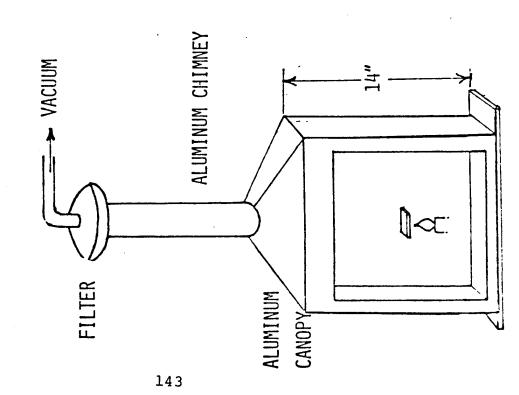
NATIONAL MORATORIUM ON OUTDOOR RELEASE OF GRAPHITE FIBERS EXCEPT UNDER RIGIDLY CONTROLLED CONDITIONS.

FACILITIES TEST RELEASE FIBER ACTIVE

- LABORATORY/EXPLORATORY NAVAL RESEARCH LABORATORY (DR. J. P. REARDON)
- CHAMBER/INTERMEDIATE NAVY DAHLGREN, VIRGINIA
 (DR. K. R. MUSSELMAN)
- OUTDOOR/RANGE TRW AF NAVY/CHINA LAKE (DR. PAUL LIEBERMAN)

LABORATORY TESTING AT NAVAL

RESEARCH LABORATORY



SAMPLE SIZE: 2" X 2" X 1/4"

FUEL: PROPANE, JP-5

EFFECTS STUDIED: COMBUSTON TIME

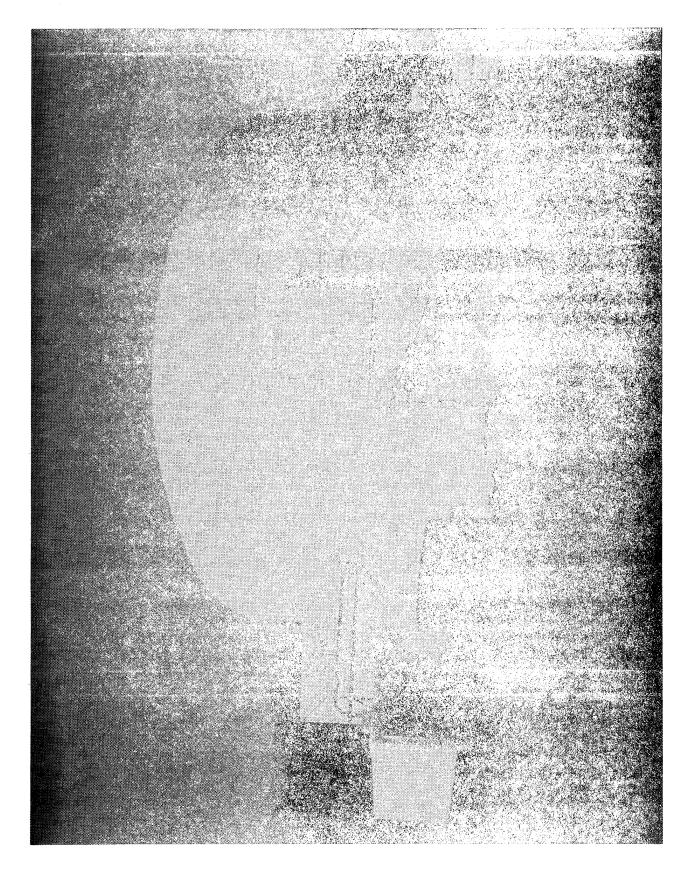
FIBER RELEASE

SPONTAMEOUS IGNITION TEMPERATURE

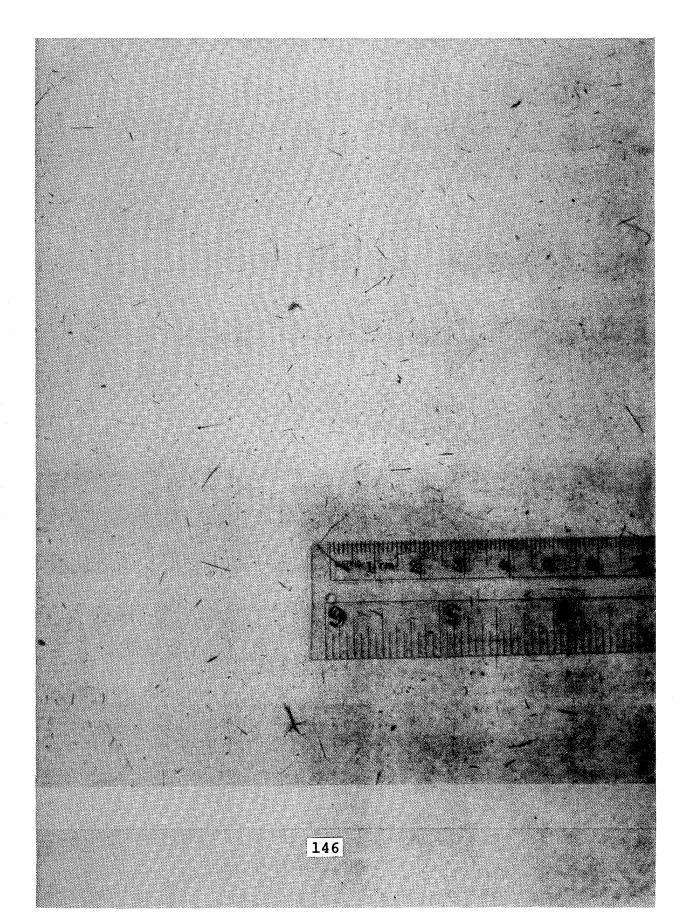
CHAR FORMATION

COMPOSITE CONSTRUCTION

ELECTRICAL PROPERTIES









CHAMBER NAVY/DAHLGREN

TEST FIXTURE:

SAMPLE HOLDER

FUEL PAN OR GAS BURNER

EXPLOSIVE DELIVERY ARM

STATIC UNBURNED/EXPLODED TEST PROCEDURES:

STATIC BURNED/EXPLODED

DYNAMIC BURNED/EXPLODED

STATIC BURNED

RESIDUE COLLECTION: GRID OF 8.9 cm PETRI DISHES (24)

0.91 m GRID - 15.2 X 20.3 cm SHEETS (107) ADHESIVE-BACKED CELLULOSE ACETATE

HAND PICKUP OF LARGE FRAGMENTS

BROOM SWEEP OF FIBROUS MATERIALS

POWER VACUUM SIVEEP

GRAPHITE FIBER MODIFICATIONS DR. R. J. DIEFENDORF, CHAIRMAN

NAME

Fred Hansen

ORGANIZATION

Roger T. Pepper	FMI Maine
Dennis Riggs	AMMRC
John Hurt	Army Research Office
J. R. Leal	Celanese Research Co.
L. H. Peebles	ONR/Boston
F. L. Vogel	Univ. of PA
H. P. Edelstein	DWT Naval Ship R&D Center
Judd Diefendorf	Renssalaer Polytechnic Institute
Brian Ence	George Washington University
J. T. Paul	Hercules Research Center
S. M. Rozowski	Ball State University
D. B. Fischbach	Univ. of Washington
D.M. Estering	George Washington University
W. D. Lee	US Army, MERADCOM
W. C. Schwemer	Vought Advanced Technology Center
C. A. Gaulin	Aerospace Corp.
R. Prescott	Great Lakes Research
Bill Chard	Battelle Columbus Lab
Guilio Varsi	Jet Propulsion Lab

NASA Reporters: W.D. Brewer and R. K. Clark, LaRC

NASA Ames

ISSUES FOR

GRAPHITE FIBER MODIFICATION

WORKING GROUP

- 1. Upon what principles might the electrical conductivity of graphite fibers be reduced?
- 2. What treatments should be investigated as applications of these principles?
- 3. For each treatment:
 - (a) What are the likely effects on fiber mechanical properties?
 - (b) What are the prospects for reducing the conductivity by a factor 10, 100, or 1000?
 - (c) What are the prospects for retention of effectiveness after exposure to the high temperature encountered in a burning composite?
 - (d) What is the likely impact on production costs?
 - (e) What will be the effect on fiber matrix bonding?
- 4. Considering the aspects raised in issue 3 above, which treatments do you recommend for detailed investigation?
- 5. Can larger diameter fibers be produced without significant reductions in mechanical properties and handleability?
- 6. Can the cross-sectional shape of the fibers be altered so that their aerodynamic characteristics would be changed?
- 7. Could selected surface imperfections be introduced so that fibers would be less resistant to fire?
- 8. Can additives be used in the precursor that would make the fibers less resistant to fire?
- 9. What is your assessment of the current NASA research program in this area, and what changes do you recommend?
- 10. Rank the different generic (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) solutions as to their probability of success.

NASA REPORTERS' SUMMARY FOR GRAPHITE FIBER MODIFICATION WORKING GROUP

Two presentations were given prior to the working group general discussions. Roger Prescott of Great Lakes Carbon gave a summary of his company's experience with graphite fibers. Donald Esterling of George Washington University discussed his plans for hydrogenation of graphite fibers for increased electrical resistivity.

The focus of the fiber modification working group was on ways to alter the electrical, oxidative, and disseminative properties of graphite fibers. In particular, emphasis was placed on ways to increase the electrical resistivity of the fibers to eliminate the electrical hazards even though the fibers may be released to the environment, and on decreasing the stability of the fibers so that they would likely burn up in a fire and not be released. Changing the size and shape of the fibers to minimize the area over which they are disseminated was discussed briefly.

At the outset, the group recognized the importance of understanding the fundamentals of electrical conductivity and oxidative properties of graphite fibers. It was also noted that better definitions are required of what levels of resistivity are acceptable and of what the exposure conditions are in an actual fire.

INCREASED RESISTIVITY

Four potential solutions to the graphite fiber problem by way of fiber modification to increase electrical resistivity were identified:

- 1. Low temperature heat treamtent
- 2. Hydrogenation
- 3. Conversion to graphitic oxide
- 4. Doping

Low Temperature Heat Treatment.— It was suggested that by heat treating at low temperatures, the defect substructure of carbon fibers could be retained while maintaining the preferred orientation necessary for good mechanical

Increasing the defect concentration should properties. significantly increase the electrical resistivity. group consensus was that this technique could readily produce changes in resistivity by a factor of 10 or 20 and possibly 100. However, changes of three orders-of-magnitude or more were considered very unlikely. In addition, it was thought that the resulting fibers could be of significantly lower-strength than those treated at higher It was also suggested that the low temperatures. temperature heat treatment results in a less stable fiber which should be consumed more readily in a fire. noted that the environment in a large pool fire is reducing (oxygen depleted) and it is doubtful that even an oxidation-susceptible fiber would be consumed. oxidation-susceptible fiber may be consumed upon inceneration of composite scrap. The question was raised as to whether or not changes in the wavelength and amplitude of the "undulating ribbons" in the fibers could affect the resistivity (crystallite scattering). For a number of reasons, the group thought that it was unlikely that ribbon changes would have any significant effect. primary reason is that the mean free path of a carrier electron is probably shorter than the shortest wavelength one could produce in a ribbon and electron interactions with other defects predominate.

The low temperature heat treatment technique was considered to be the most advantageous as far as manufacturing is concerned. In fact, the carbon producers indicated that such a process would be welcomed and would have little impact on the cost of the fibers.

Hydrogenation of Fibers. - Electrical conduction is thought to be associated, in part, with the migration of electron holes created by surface defects such as unsatisfied chemical bonds, improperly coordinated atoms, etc. Those defects tend to trap electrons, creating holes by which electricity can be conducted. It was suggested that if these traps can be eliminated, the resistivity can be significantly increased. The procedure would be to introduce hydrogen into the fibers, to lock onto those dangling bonds, thus removing acceptor sites and The details of the hydrogenation eliminating the holes. procedure were not defined; however, it is likely that the fibers would be exposed to a hydrogen atmosphere at about 1000°C and 1 or 2 atmospheres pressure for about 1/2 hour. It could not be said whether or not there would be any effect, but the effect, if present could potentially be large.

The working group was not aware of any successful attempt to hydrogenate graphite. The question was also

raised as to whether the hydrogenation process would be reversed in a fire. No one had anything firm to say about this question, but it was thought that if the hydrogen could be put in, it would probably stay.

The carbon manufacturers noted that whatever process was used, it would not be cost effective because of the hazards of working with hydrogen at high temperatures. They felt that, at present, hydrogenation would not be a viable approach from the manufacturing standpoint. The feeling of the group was that this approach had a small probability of success, but encouraged continuation of the work.

Conversion of Fibers to Graphitic Oxide.— The general procedure is to expose fibers to strong oxidizing solutions for a few minutes. The oxygen apparently enters between the graphite layers, locks onto loose double bonds, and eliminates current carriers. There are two positive features about this approach. First, available literature indicates that increases in resistivity of several orders of magnitude are possible.

Second, the graphitic oxide may be inherently less stable and burn up in a fire. Even if the exposure conditions were reducing, the fiber itself may be a sufficient source of oxygen to cause it to burn. The question was raised as to whether this instability would allow the fiber to survive fabrication. No one could say with any confidence what would happen in fabrication or in a fire. The major concerns about this approach were the instability and possible degradation of mechanical properties. At present, these are unknown factors.

The graphitic oxide approach would be expensive, again because of working with potentially explosive mixtures. However, the problems could probably be overcome in a production process.

In general, the group considered the graphitic oxide approach to have some promise. There were some suggestions to investigate perhaps fluorine, nitrogen or sulfur in addition to oxygen.

Doping. This approach attempts to remove positive or negative carriers by introducing electron donor or acceptor atoms into the graphite structure. Doping was suggested, but was discussed very little by the group. It was suggested that there were some dopants such as nitrogen or boron and nitrogen together which could be beneficial.

DECREASED STABILITY AND CHANGES IN SHAPE AND SIZE

The group felt that introducing additives into precursors or introducing surface imperfections in fibers are probably not viable approaches for making fibers less resistant to fires. Surface imperfections would no doubt degrade fiber strength significantly and precursor additives may not be effective in a reducing (oxygen depleted) atmosphere.

The working group briefly considered changing the shape and size of fibers to alter the aerodynamic characteristics. It was decided that a circular cross-section fiber would have the greatest fall rate, and there is no incentive to produce fibers with different shapes. Fiber diameter could be increased by a factor of 2 while maintaining reasonable mechanical properties, probably without greatly affecting cost. However, producing fibers with changes in diameter greater than a factor of two would be prohibitively time consuming and costly.

In general, the potential solutions proposed by the Fiber Modification Working Group were not considered to be short term fixes. The expected time frame and cost for conducting feasibility studies, process development, and materials qualification program for just one approach was considered to be 2-5 years and \$2M.

CONCLUSIONS

- 1. Fiber modification does not hold much promise for complete solutions to the graphite fiber problems.
- 2. Of the potential solutions discussed, the graphitic oxide appears to have the best chance of success in meeting electrical requirements.
- 3. Changes in fiber resistivity by a factor of 10 are achievable. Changes of more than two orders of magnitude are unlikely.
- 4. Introducing additives to reduce fiber stability is probably not a viable approach.
- 5. Changing size and shape of fibers is not likely to significantly improve the fall rate characteristics.
- 6. The proposed potential solutions are not short term fixes even if they work. The expected time frame and cost for just one approach to be fully developed is considered to be 2-5 years and \$2M.

RECOMMENDATIONS

- 1. Continue concentrated research efforts in all the areas discussed.
- 2. Research should be conducted by university, government or other research labs (as opposed to fiber manufacturers).
- 3. Fiber manufacturers should be consulted and become actively involved when the feasibility of an approach has been demonstrated.
- 4. Rapid and effective information transfer between persons and organizations working on graphite fiber modification should be maintained through:
 - (a) informal bimonthly newsletters
 - (b) group meetings of actual researchers

REPORT OF

GRAPHITE FIBER MODIFICATION WORKING GROUP

R. J. DIEFENDORF, CHAIRMAN

GRAPHITE FIBER MODIFICATIONS

O LOW TEMPERATURE HEAT TREATMENT

o DOPING

O HYDROGENATION

O GRAPHITIC OXIDE

DISCUSSION TOPICS

(TECHNICAL)

O CONDUCTIVITY

o OXIDATION

DISSEMINATION

CHARGE CARRIER (WHERE FROM?)

0

- GRAPHITE 0
- FEW CARRIERS HIGH MOBILITY
- CARBON 0
- MANY CARRIERS LOW MOBILITY

POSSIBLE SOLUTIONS

- O DOUBLE BONDS GRAPHITIC OXIDE
- DANGLING BONDS
 HYDROGENATE
- NITROGEN COMPENSATION
- O LOW TEMPERATURE HEAT TREATMENT
- CRYSTALLITE SCATTERING

PROBABILITY OF CONDUCTIVITY CHANGE

10 X -

FAIR 100 X -

POOR

1000 X -

FIRE SURVIVABILITY

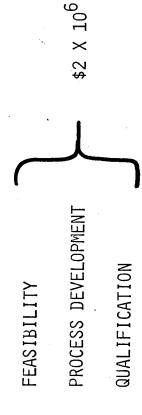
(REDUCING CONDITIONS)

- HIGHER OXIDIZABILITY
- O LOWER HEAT TREATMENT TEMPERATURE
- o ADDITIVES

IBER DISSEMINATION

- SHAPE ROUND BEST
- O MASS LARGER DIAMETER

COSTS PER MODIFICATION



INFORMATION TRANSFER

O BIMONTHLY INFORMAL REPORTS

O GROUP MEETINGS

ANKING OF GENERIC SOLUTIONS

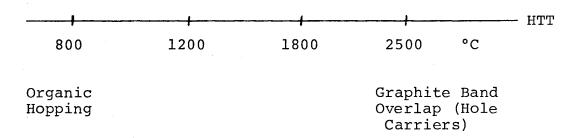
I - 3 BASIS)

	RANK
FIBER MODIFICATION	1,94
FIBER COATING	1,82
ALTERNATE FIBERS	1,35
EPOXY MODIFICATION	2,53
EPOXY REPLACEMENT	2,53
HYBRIDS	1,71

HYDROGENATION OF CARBON FIBERS

by

D. M. Esterling
The George Washington University



What are charge carriers?

What is conduction mechanism?

How are the carriers introduced?

(Band overlap vs. defects vs. impurities (N))

Different answers for different HTT.

Sensible way to decrease of for HTT 2,500 °C (e.g. introduce impurities) may be exactly wrong at HTT of 1400 °C.

High HTT - High mobility, few carriers (Little hope, only small changes in σ at best).

Low HTT (< 1800 °C) - lower mobility, many carriers.

Electron states

- Gap?
- Continuous $\begin{cases} \text{Localized} \, (\text{Mott/Anderson}) \\ \text{Delocalized} \end{cases}$

Conduction - Holes in disordered system

Origin of holes - acceptor sites of unknown origin (electron traps)

- Surface?
- {Dangling Bonds?
 Improperly coordinated atoms?

Remove electron traps by eliminating defects.

Hydrogen Bonds - Saturate dangling bonds (fill electron trap with electron that is not coming from carbon chain)

- Why not dope with donor atoms (alkalais)
- Really looking for <u>chemical</u> effect (<u>Local</u> change in structure). Dopants give global change in electron density.

How?? 900° - 1000 °C @ 1 ATM H₂ (No Catalyst)
400° - 500 °C @ 1 ATM H₂ (Catalyst)

GRAPHITE FIBER COATING & ALTERNATIVE FIBERS Dr. James Economy, Chairman

NAME

ORGANIZATION

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General Dynamics

Celanese Research Co.

Fiber Materials, Inc.

Jet Propulsion Lab.

NASA Ames

General Electric Co.

NASA Marshall

Army Mat. & Mech. Research Center

Naval Surface Weapons Center

Washington State University

AVCO Specialty Materials

Bell-Helicopter Textron

Union Carbide Corp.

McDonnell Douglas Corp.

NASA Reporters: S. S. Tompkins and C. M. Pittman, LaRC

ISSUES FOR

GRAPHITE FIBER COATING ALTERNATIVE FIBERS

WORKING GROUP

- 1. What high electrical resistance coatings can be applied to graphite fibers? How thick would they need to be? What coating method would be employed?
- 2. Which of these coatings is likely to remain intact after fire and explosion?
- 3. Which of these coatings can be readily applied during the fiber manufacturing process?
- 4. What precursor coatings can be applied that would convert to a high electrical resistance coating in-situ during fire and explosion?
- 5. What coatings can be applied that might result in fiber "clumping" as a result of exposure to fire and explosion?
- 6. For all types of coatings considered, what is the likely effect on fiber-matrix bonding?
- 7. What other fibers (e.g., BN, Kevlar, SiC) should be considered as alternatives to graphite? What are their advantages and disadvantages?
- 8. Rank the potential replacement fibers as to the probability that they could be incorporated into the ACEE program.
- 9. Would hollow glass or graphite fibers be worth developing as a potential solution?
- 10. What is your assessment of the current NASA research program in this area, and what changes do you recommend?
- 11. Rank the different generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS SUMMARY FOR FIBER COATINGS AND ALTERNATIVE FIBERS WORKING GROUP

Four presentations preceded the working group open discussions. Kumar Ramokalli discussed work at JPL on coating graphite fibers to increase electrical resistivity as well as to promote clumping of fibers to reduce their dissemination. R. V. Subramanian of Washington State University discussed an electrolytic technique for coating fibers with a polymer. Robert Hamilton of Carborundum discussed his company's development of a BN fiber. Ashok Dhingra gave a report on DuPont's development of Kevlar and FP (Al₂O₃) fibers as possible replacement for graphite.

COATINGS

The working group discussions of coatings were directed toward four areas:

- Inorganic coatings SiC, B, B₄C, BN, Si₃N₄, SiO₂
- 2. Organic and metallorganic coatings to provide a high density char layer on the fiber surface.
- 3. Metallic coatings Al, Cr, Ni
- 4. Catalytic coatings to increase the fiber oxidation rate.

Items 1 and 2 received the most attention. The rationale for using metallic coatings, item 3, was the possiblity of forming a metal oxide on the fiber surface during a fire. However, considerable doubt was expressed as to whether sufficient oxygen would be available to form the oxide. Catalytic coatings, item 4, were thought to be more in the province of the fiber modification working group and were only briefly discussed.

Inorganic Coatings. - The consensus of the working group was that the inorganic coating work, underway or being initiated, includes the most promising coating materials. These coating materials include:

- 1. Sic
- 2. B
- 3. B₄C
- 4. BN
- 5. Si₃N₄
- 6. Sio₂
- Metallic silicates

The working group felt that the coating efforts should critically examine:

- 1. The effect of the coating on composite mechanical properties.
- 2. The effect of the coating on fiber release, fall rate, and electrical properties.
 - 3. The effect of the coating on cost.
 - 4. The chemical stability of nitride coatings.

Organic Coatings Which Char. The objective of this work is to find an organic coating which, when charred, would facilitate fiber clumping and/or act as an insulative coating. The coating must have a high char yield and also provide an effective fiber-matrix bond. The group encouraged continued work on silicones, high temperature polymers such as polybenzimidazole (PBI) and polyphenylquinoxoline (PPQ) and evaluation of new techniques of electrolytic polymer coating deposition.

Alternate Fibers

The alternate fibers which were discussed included:

- 1. BN fibers
- 2. High modulus organic fibers
- 3. αAl₂O₃ (FP fibers from DuPont)
- 4. SiC both large and small diameter fibers
- 5. B fibers with a carbon core
- 6. Glass fibers
- 7. B_AC fibers
- 8. 33 μm carbon fibers
- 9. AlB₂ flakes

These alternate fibers are listed more or less in the order in which the working group felt that the fibers showed the most promise. Boron and glass fibers were not discussed extensively. The general consensus was that these fibers are available and should be considered for some applications. The large diameter carbon fibers, item

8, were mentioned because of their potential for increasing the fiber fall rate, however, their mechanical properties would require substantial improvement. The AlB₂ flakes were mentioned in connection with a hybrid composite of AlB₂ flakes and carbon fibers. This approach could reduce the amount of carbon fibers and, therefore, reduce the risk.

BN Fibers. - Carborundum has prepared small experimental samples of BN fibers with the following properties.

E = 30-50 Msi

 $\sigma = 300 \text{ ksi}$

 $\rho = 1.8 \text{ g/cc}$

The primary advantage of BN fibers is that they are very similar to carbon fibers and therefore, would probably perturb the present composite technology less than any other alternate fiber. The main disadvantage of BN fibers is that at least 4-5 years of work would be required to develop a commercial fiber at the present research pace.

High Modulus Organic Fibers. - DuPont has five new experimental fibers with the following properties:

E = 20-30 Msi

 $\sigma = 300-600 \text{ ksi}$

 $\rho = 1.22 - 1.48 \text{ g/cc}$

One or more of these fibers could replace carbon in some applications. However, these fibers have poor compression properties, and composite fabrication technology would require development. The working group recommended that these fibers be evaluated in hybrid configurations because of the low fiber modulus.

 α Al $_2{\rm O}_3$ (FP) Fibers. -DuPont has developed Al $_2{\rm O}_3$ yarn which is cost competitive with carbon fiber and has the following properties:

E = 55 Msi

 $\sigma = 200$ ksi (300 ksi expected with smaller diameter)

 $\rho = 3.9 \text{ g/cc}$

diameter = $20 \mu m$

This fiber could be commercially available in the very near future. The disadvantages of FP fibers are their high density and brittleness. The recommendation of the working group was to evaluate FP fibers in hybrids in an attempt to improve composite fracture strain.

SiC Fibers. - AVCO has developed a 130 µm SiC (carbon core) fiber with the following properties:

E = 50-60 Msi $\sigma = 500$ ksi $\rho = 3.2$ g/cc

The advantages of this fiber are its excellent mechanical properties. The disadvantages are the large fiber diameter and high density. The working group recommended that these fibers be evaluated in hybrid composites and that a small diameter SiC fiber be developed. (Japan has reportedly developed a small diameter SiC fiber.)

B₄C Fibers .- A continuous filament B₄C yarn, with the following properties has been reported:

E = 40-55 Msi $\sigma = 300-400$ ksi $\rho = 2.28$ g/cc yarn - 720 ends, 9 μ m diameter

The advantages of this yarn are that the properties are similar to carbon fibers. The disadvantages are that only a laboratory process has been defined and 2-3 years are required for scale-up. Also the fibers will be more expensive than carbon. The working group recommended that a cost analysis, including production scale-up, be made to determine $B_{\Delta}C$ fiber feasibility.

CONCLUSIONS

- 1. No particular coating is presently favored over any other.
- 2. No coating should be eliminated without more information and tests.
- 3. BN fibers should be considered a long term substitute for carbon. Other alternate fibers should only be considered for hybrid composites.

- 4. Any change in fiber or coating is necessarily a long term solution (3-5 years).
- 5. A critical lack of quantitative information on the properties required to alleviate the electrical hazard is apparent. For example:
- a. How much must the overall fiber resistance be increased?
- b. How much fiber clumping is required and how many fibers make a clump?
 - c. How much must the settling rate be increased?

Answers to these and similar questions should be obtained as soon as possible so that the research effort can proceed toward known objectives.

RECOMMENDATIONS

The working group made the following recommendations.

Continue work on:

- 1. Inorganic coatings
- 2. Organic coatings
- 3. Organometallic coatings
- 4. BN fibers

Initiate programs on:

- l. Hybrid composites of high modulus organic fibers with B (carbon core) fibers, SiC (carbon core) fibers and Al_2O_3 (FP) fibers.
 - 2. Producing small diameter SiC fibers.
 - 3. BAC yarn cost analysis and production scale-up.

REPORT OF

GRAPHITE FIBER COATING & ALTERNATIVE FIBERS WORKING GROUP

Dr. JAMES ECONOMY, CHAIRMAN

GRAPHITE FIBER COATING AND ALTERNATIVE FIBERS

```
INORGANIC: SiC, B, B4C, BN, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>
ORGANIC/METALLORGANIC: HIGH CHAR
```

ORGANI C/METALLORGANIC:

METALLIC: Al, Cr, Ni

CATALYTIC: OXIDATION OF CARBON

SEVERAL POINTS OF CONCERN

ALTERNATIVE FIBERS

HIGH MODULUS ORGANICS

A A1₂0₃(FP)
 Sic LARGE, SMALL DIAMETER

B(CARBON CORE)

GLASS

INORGANIC COATINGS

O PROGRAMS INITIATED AT JPL, AVCO, UTC AND UCC ON

 $\begin{array}{c} \text{SiC} \\ \text{B} \\ \text{B} \\ \text{BN} \\ \text{Si}_{3} \text{N}_{4} \\ \text{M}_{2} \text{Si}_{2} \text{O}_{3} \end{array}$

- O CRITICAL ISSUES
- COATING THICKNESS VS, VOLTAGE
- EFFECT ON STRENGTH
- CHEMICAL STABILITY OF NITRIDES
- POTENTIAL FOR CLUMPING
- COATING PROCESS/COST

ORGANIC COATINGS WHICH CHAR

WOULD BE REQUIRED FOR CHAR FORMING MATRIX 0 PURPOSE:

O MAY FACILITATE CLUMPING

CHAR MAY ACT AS INSULATOR

REQUIREMENTS: 0

HIGH CHAR YIELD

EFFECTIVE FIBER-MATRIX BOND

0

RECOMMENDATIONS:

o CONTINUE STUDIES ON SILICONE

o EVALUATE HIGH TEMPERATURE POLYMERS AS COUPLERS, PBI, PPQ

O EVALUATE NEW TECHNIQUES TO IMPROVE INTERLAMINAR SHEAR PROPERTIES, ELECTROLYTIC POLYMERIZATION

HIGH MODULUS ORGANIC FIBERS

DUPONT HAS FIVE NEW EXPERIMENTAL FIBERS

20 - 30 msi ليا

300 - 600 ksi

© 1.22 - 1.48 g/cc

COULD REPLACE CARBON IN CERTAIN AREAS ADVANTAGES:

POOR COMPRESSION PROPERTIES, BONDING DISADVANTAGES:

EXPLORE IN HYBRIDS. RECOMMENDATION:

BN FIBERS

CARBORUNDUM HAS PREPARED SMALL EXPERIMENTAL SAMPLES OF HIGH MODULUS BN FIBERS

30 - 50 Msi

7 300 ksi

1,8 g/cc

BN FIBER IS VERY SIMILAR TO GRAPHITE

ADVANTAGES:

4 - 5 YEARS OF DEVELOPMENT REQUIRED AT PRESENT PACE DISADVANTAGES:

PLAN: NASA/ONR PLANNING JOINT SUPPORT

$\mathbf{A}_{A1_20_3}$ (FP)

Dupont has developed ${\rm A1_20_3}$ yarn cost competive with graphite fiber

55 Msi

6 200 ksi (300 ksi SEEN)

6 3,9 g/cc

DIAMETER 20 Am

AVAILABLE IN VERY NEAR FUTURE

ADVANTAGES:

DISADVANTAGES: HIGH DENSITY, BRITTLENESS

RECOMMENDATIONS: EVALUATE IN HYBRID IMPROVE FRACTURE STRAIN

AVCO HAS DEVELOPED A 130 AM SIC (C-CORE) FILAMENT

50 - 60 Msi ш

9 500 ksi

6 3.2, g/cc

EXCELLENT MECHANICAL PROPERTY

ADVANTAGES:

DIAMETER AND DENSITY

DISADVANTAGES:

EVALUATE IN HYBRID DEVELOP SMALL DIAMETER TOW

RECOMMENDATIONS:

B4C YARN

A CONTINUOUS FILAMENT YARN HAS BEEN REPORTED

40 - 55 Msi ш

6 300 - 400 ksi

Q 2.28 g/cc

YARN 720 ENDS, 9 m DIAMETER

ADVANTAGES:

SIMILAR IN PROPERTIES TO GRAPHITE

DISADVANTAGES:

LAB PROCESS DEFINED BUT WILL REQUIRE 2 - 3 YR, SCALE-UP, COST GRAPHITE

RECOMMENDATION:

CARRY OUT COST ANALYSIS

RECOMMENDATIONS

CONTINUE PLANS WITH

- O INORGANIC COATINGS
- O ORGANOMETALLIC COATINGS
- O BN FIBERS

INITIATE PROGRAMS ON

- O HIGH CHAR YIELD ORGANIC COATINGS
- o HYBRID OF HIGH MODULUS ORGANICS WITH B (CARBON CONE), SIC (CARBON CORE) Al₂0₃ (FP)
- o B_{4} C YARN SCALE-UP
- O LOW COST SIC TOW

ORGANIC FIBERS AND HYBRID COMPOSITES

ASHOK DHRINGRA E.I. DuPONT

MARCH 23, 1978

EXPERIMENTAL HIGH MODULUS ORGANIC FIBERS

Properties of certain experimental organic fibers exhibiting very high strengths and high moduli will be discussed. These have tensile strengths ranging from 400 Kpsi to 600 Kpsi and tensile moduli ranging from 25 to 30 x 10^6 psi. Fiber densities are low and range from 1.22 to 1.46 g/cc. These fibers should be of interest in composites provided an effective transfer of their properties into laminates can be achieved.

FP/KEVLAR® AND GRAPHITE/KEVLAR® HYBRID COMPOSITES

An experimental inorganic aluminum oxide fiber designated Fiber FP is currently under development in the Du Pont Company. This fiber is characterized by high modulus, outstanding compressive strength, hydrolytic and chemical stability and nonconductivity. Combining Fiber FP or graphite with Kevlar® aramid fiber produces hybrid composite structures having significantly improved combination of properties not attainable with single fibers. The properties of FP/epoxy, FP/polyimide, FP/Kevlar®/epoxy hybrid and Graphite/Kevlar®/epoxy hybrid will be discussed.

POSSIBLE SOLUTIONS

NEW FIBERS

- 1. HIGHER MODULUS ORGANIC FIBERS (BEYOND KEVLAR®)
- 2. HIGHER TENSILE STRENGTH FP FIBER
- LOWER DENSITY INORGANIC FIBER (MODIFIED FP)

MODULUS

40MM PSI

STRENGTH

300 Kpsi

ELONGATION

0.8%

APPROACH

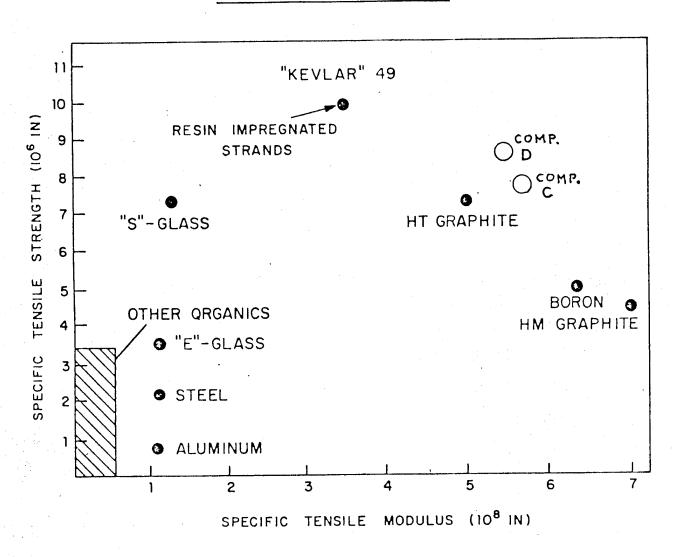
HYBRID COMPOSITES

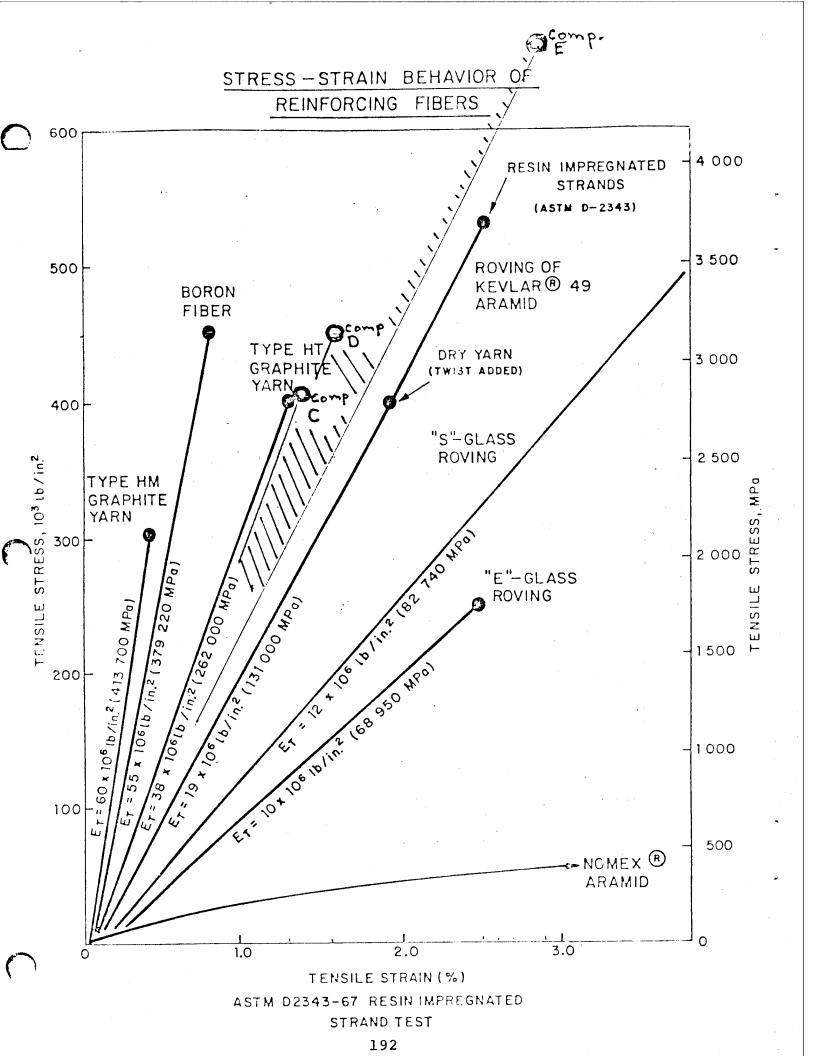
EXPERIMENTAL HIGH MODULUS ORGANIC FIBERS

	Density $(1b/1n^3)$	Tensile Strength (Kpsi)	Tensile Modulus (10 ⁶ psi)	Specific Strength (10 ⁶ in)	Specific Modulus (10 ⁸ in)	How Tested
Composition A	.052	341	25.8	9.9	5.0	10 in. yam
Composition B	,052	336	27.4	6.5	5.3	10 in. yarn
Composition C	.052	408	29.6	7.8	5.7	10 in. yarn
Composition D	.052	450	. 28,8	. 8.7	5.5	10 in. yarn
Composition E	ħħ0 °	1 799	.20.5	15.1	2.4	10 in. yarn in resin

COMP.

SPECIFIC TENSILE STRENGTH AND SPECIFIC TENSILE MODULUS OF REINFORCING FIBERS





MECHANICAL PROPERTY COMPARISON FP/KEVLAR® 49/EPOXY -VS- KEVLAR® 49/EPOXY

PROPERTY	KEVLAR®/EPOXY (60/40)	FP/KEYLAR®/EPOXY (30/30/40)	CHANGE
COMPRESSIVE MODULUS, MPSI	11.5	21	1.8X
COMPRESSIVE STRENGTH, KPSI	40	150	3.75X
TENSILE MODULUS, MPSI	14	20	1.4X
TENSILE STRENGTH, KPSI	193	148	-23%

• COMBINING FP WITH KEVLAR® GREATLY

IMPROVES STIFFNESS AND COMPRESSIVE

STRENGTH

TABLE II

PROPERTIES OF UNIDIRECTICNAL "THORNEL" 300, "KEVLAR" 49 AND HYBRID COMPOSITES - NOMINAL FIBER VOLUME FRACTION = 0.60

				Compression	ssion	Fle	Flexure	Short	
Percentages of		Tension	uc	Stress		Stress		Beam	
"Thornel" 300/			Ultimate	at 0.02%	Ultimate	at 0.02%	Ultimate		Prepreg
"Kevlar" 49	Specific*	Modulus	Stress	Cffset		Offset	Stress	Stress	Cost
Fibers	Gravity	(TSd ₀₀ T)	(KSI)	(KSI)	(KS1)	(KSI)	(KSI)		9/10
0/001	1.60	21.1	227	98.4	146	233	233	13.2	09
75/25	1.56	17.4	186	68.8	136	181	197	11.0	48
50/50	1.51	15.7	176	59.9	8.66	120	160	8.1	35
0/100	1.35	11.2	183	26.4	41.5	49.2	91.9	7.1	on of

*Data supplied by Fiberite

TABLE III

MECHANICAL PROPERTIES OF "KEVLAR" 49-"THORNEL" 300 HYBRID BALANCED FABRIC COMPOSITES

Tension and Compression Data Normalized to 65% Fiber Volume Fraction

Short Beam Shear Strength	3.8	4.2	4.7	5.8	7.0
Compressive Stress 0.028 [ffset Ultimate 0.3 psi) (103 psi)	22	33	46	81	42
Compress: At 0.02% Offset	11.0	23	32	47	24
Tensile Strength (10 ³ psi)	79	بر 8	63	63	09
Modulus (106 psi)	5.2	7.0	8.3	8.7	6.7
Specific Gravity	1.40	1.49	1.57	1.60	1.44
Resin	Fiberite 934	=	=	=	BP-907
Ratio of "Kevlar" 49-to-"Thornel" 300	100/0	50/50	25/75	0/100	50/50
	1	95			

TABLE VI

MECHANICAL PROPERTIES OF "KEVLAR" 49-"THORNEL" 300 HYBRID UNIDIRECTIONAL FABRIC COMPOSITES

Tension and Compression Data Normalized to 65% Fiber Volume Fraction Short

Beam	Shear Strength (10 ³ psi)	7.9	8
Compressive Stress	Ultimate (10 ³ psi)	52	56
Compress	At 0.02% Offset (10 ³ psi)	32	7
	Tensile Strength (10 ³ psi)	103	104
	Modulus (10 ⁶ psi)	12.6	11.3
	Specific	1.44	1.40
	Resin	Fiberite 934	BP-907
	Ratio of "Kevlar" 49-to- "Thornel" 300	50/50	50/50
	= X =	<u> </u>	196

TABLE V

NOTCH SENSITIVITY OF [6/90] AS GRAPHITE-"KEVLAR" 49 HYBRID COMPOSITES

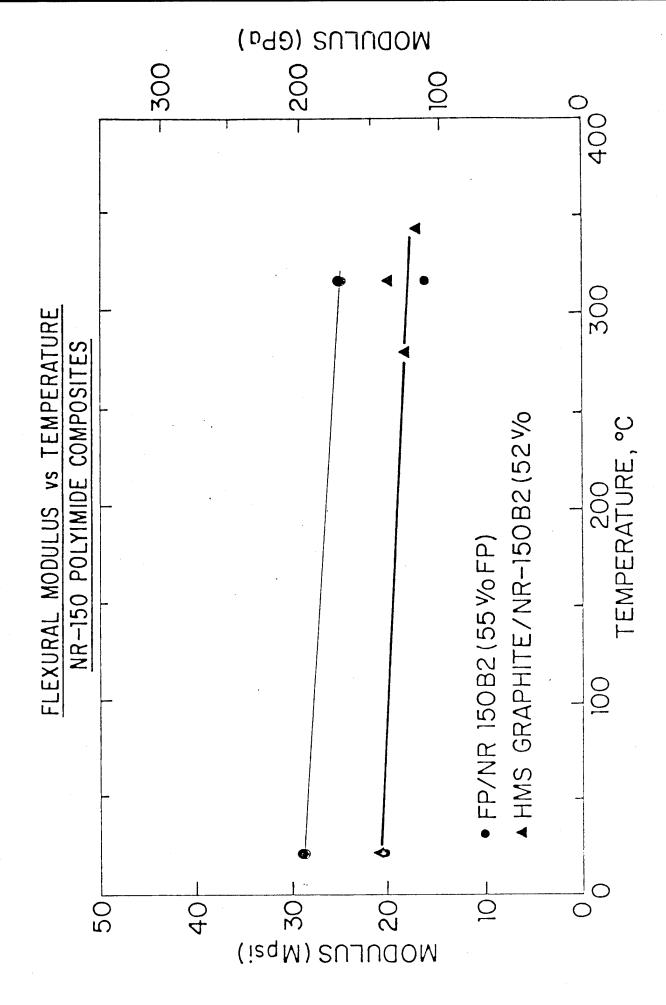
Nominal Crack Modulus Thick. Length		AS Graphite (Tape) 7.67 0.048 0	0.048 0.25	12-Ply 7.87 0.072 0	0.072 0.25	"Kaylar" 49 4.17 0.030 0	(Style 120 Fabric) 0.030 0.25	Hybrid (8 Plies 6.32 0.078 0	of Graphite Tape + 4 Plies of "Kevlar" 0.078 0.25 43 Fabric)
Stress at Failure Gross Ne	(ksi)	75.8	14.88	78.5	15.31	72.9	25.2	66.5	20.2
s at lire Net On	(ksi)	75.8	19.88	78.5	20.5	72.9	34.3	66.5	27.0
Fracture Toughness K	(ksi-in1/2)	1	9.37	1 1	99.6	ł	16.16	1	12.75
Stress Concentration Factor	×	ŧ	3.82	3 1	3.82	ŝ ŧ	2.13	1	2.46

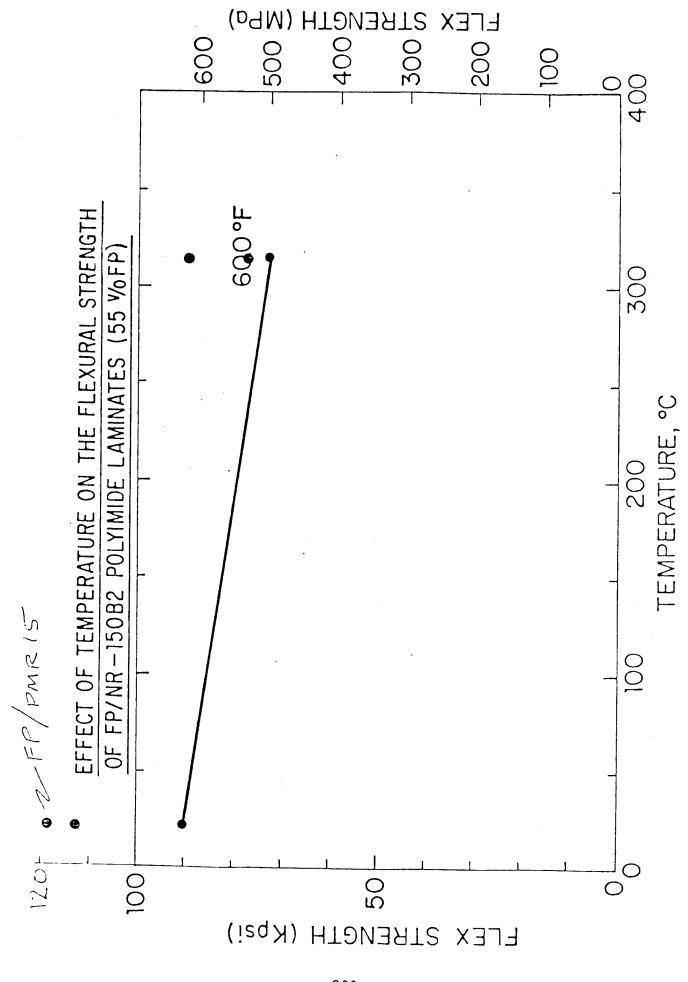
MECHANICAL PROPERTY COMPARISON OF HYBRID COMPOSITES

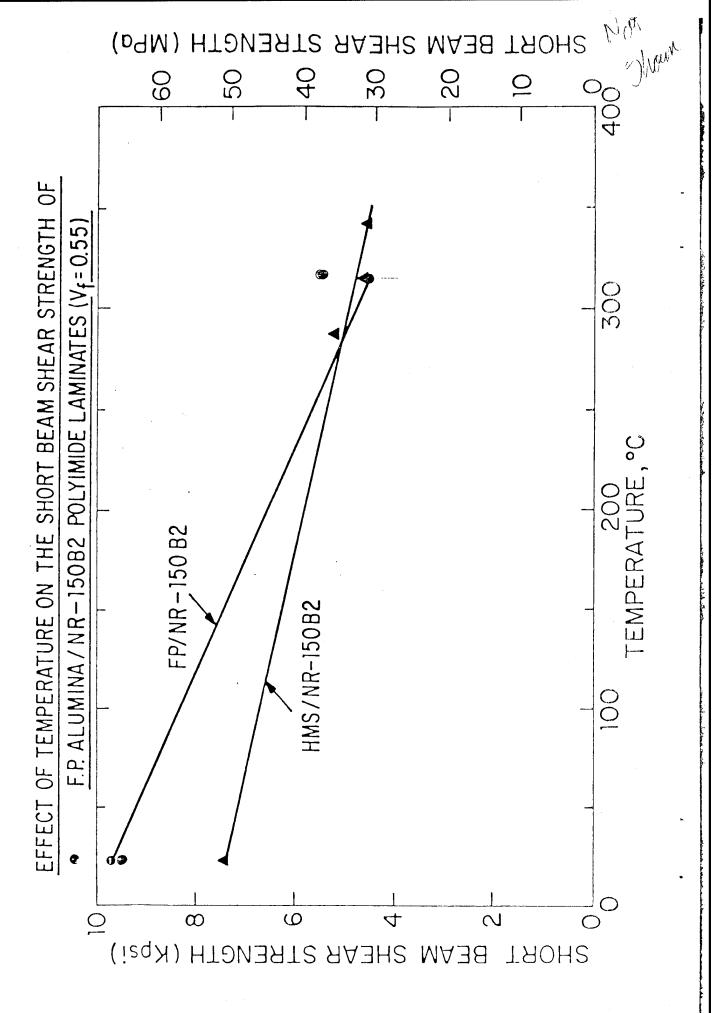
/EP0XY TH 300/EP0XY +0) (60/40)	21	227	21	146	233	7,1 13,2	1,35 1,60 ,049 ,058
KEVLAR®/EPOXY (60/40)		183	11	0†	92		
FP/KEVLAR®/EPOXY (30/30/40)	20	148	21	150	180	0.0	1,95
KEVLAR®/TH 300/EPOXY (30/30/40)	16	176	16	100	160	8.1	1,51
PROPERTY	TENSILE MODULUS, MPSI	TENSILE STRENGTH, KPSI	COMPRESSIVE MODULUS, MPSI	© COMPRESSIVE STRENGTH, KPSI	FLEXURE STRENGTH, KPSI	SHORT BEAM SHEAR, KPSI	DENSITY, G/Cm ³ (LB/IN ³)

SPECIFIC PROPERTY COMPARISON OF HYBRID COMPOSITES

Тн 300/EP0XY (60/40)	3,62	3,91	3,62	2,52
KEVLAR®/EPOXY (60/40)	2,24	3,73	2,24	0,82
FP/KEVLAR®/EP0XY (30/30/40)	2,86	2,11	3,0	2,14
KEVLAR®/TH 300/EP0XY (30/30/40)	2.91	3,2	2,91	1,82
SPECIFIC	SPECIFIC TENSILE MODULUS, 10 ⁸ IN	SPECIFIC TENSILE STRENGTH, 10 ⁶ IN	SPECIFIC 66 COMPRESSIVE MODULUS, 108 IN	SPECIFIC COMPRESSIVE STRENGTH, 10 ⁶ IN







BORON NITRIDE FIBERS ROBERT S. HAMILTON THE CARBORUNDUM COMPANY

MARCH 23, 1978

<u>Dielectric Properties</u> - The dielectric properties of boron nitride composites using boron nitride fiber are displayed in Table 3.

CHEMICAL PROPERTIES

Acid-Base Stability - Boron nitride is very stable to acidic and basic medium. Table 4 compares the weight loss upon refluxing for boron nitride fiber, carbon fiber and Pyrex fibers. Also, included in Table 4 is the action of room temperature hydrofluoric acid on these fibers. Boron nitride fibers shows 0.1% weight loss after 75 hours exposure to 100°C water. A loss of 0.8% after 1 hour of 700°C steam. Boron nitride fibers are also stable in melts of silicon, copper, cryolite, sodium chloride, lithium chloride, potassium chloride mixtures and molten cast iron and aluminum.

PREPARATION OF BORON NITRIDE FIBER

Boron nitride fiber is currently prepared by the method of Economy and Anderson as patented in 1972 (U.S. #3,668,059).

The three step process:

- 1. Fiberization of a boric oxide melt.
- 2. Nitriding of the boric oxide fiber.
- 3. Orientation/stabilization of the nitrided boric oxide fiber

where Step 1 uses commercially similar fiber glass drawing techniques. Step 2 is a unique gas phase - solid phase chemical conversion step and Step 3 is similar to processing used to produce high performance graphite fiber.

Process Chemistry - The chemistry of Step 2 and 3 can be expressed as:

$$nB_2O_3$$
 (fiber) $\frac{NH_3}{2000C}$ (B_2O_3) $n.NH_3$ Eq. 1

$$(B_2O_3)_n.NH_3 \xrightarrow{NH_3} (BN)_x (B_2O_3)_y.(NH_3)_z + H_2O$$
 Eq. 2

$$(BN)_{x}(B_{2}O_{3})_{y}.(NH_{3})_{z} \xrightarrow{2200^{O}C} BN \text{ (fiber)} Eq. 3$$

+ $B_{2}O_{3} + H_{2}O + NH_{3}$

with Equation 1 and 2 describing the gas phase — solid phase chemical nitriding of boric oxide fiber of Step 2 and Equation 3 describing the Purification/Stabilization process of Step 3. The reactions of Equation 1, diffusion of ammonia into the solid boric oxide fiber and the diffusion of $\rm H_{2}O$

Test Speed .02 in/min.
Gage Length 1.00 in.

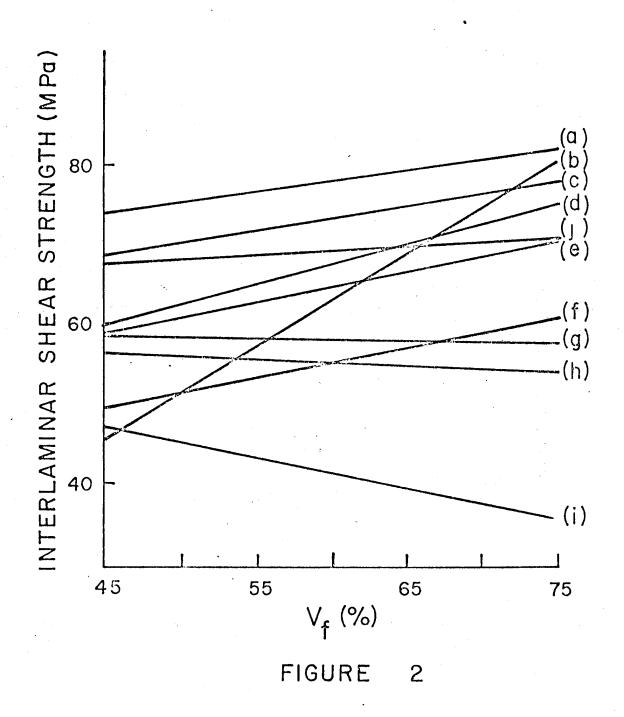
Diameter		Stress	Módulus
(Microns		(psi)	(psi)
4.03		106736	31158036
4.48		145736	30398249
4.10		170063	22093583
3.75		162268	46708458
5.37		65131	26168747
3.30		337774	50896127
3.36		76766	24459884
3.94		103412	32176816
3.54		135765	26929805
3.98		109705	27147841
4.87		62571	26453153
3.56		175463	43466871
3.63		99009	26484057
3.30		116473	32446280
3.46		176578	41304888
3.96		106305	33588282
3.30		91515	53704189
3.52		99444	30968947
4.25		64992	23753659
3.72		75579	25623728
4.22		34529	11852551
3.92		86949	28640527
Mean	Dev.	118307	31655667
Std.		62810	9981718

Table 5. Boron Nitride Fiber Tensile Test (Fiber Stretched 30%)

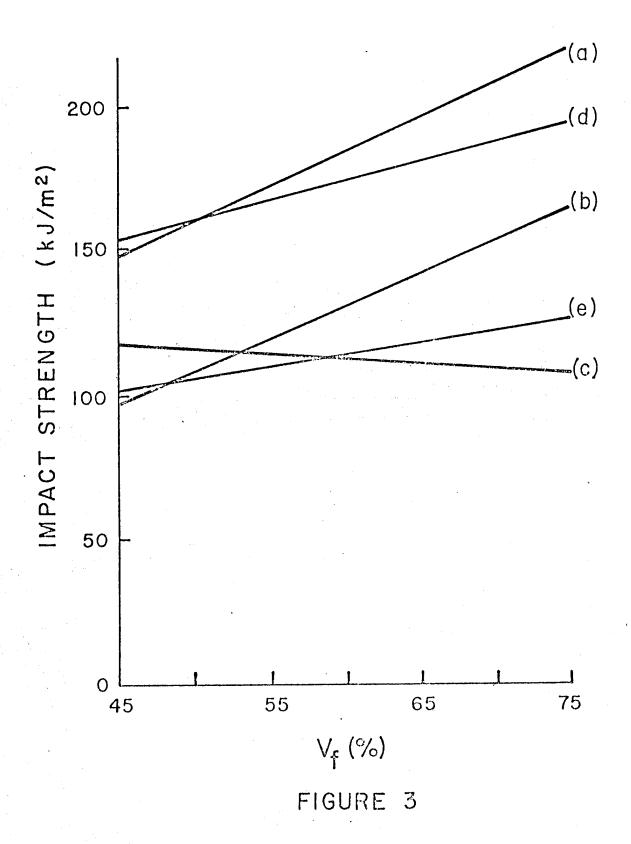
ELECTRODIC COATINGS

R. V. SUBRAMANIAN WASHINGTON STATE UNIVERSITY

MARCH 23, 1978

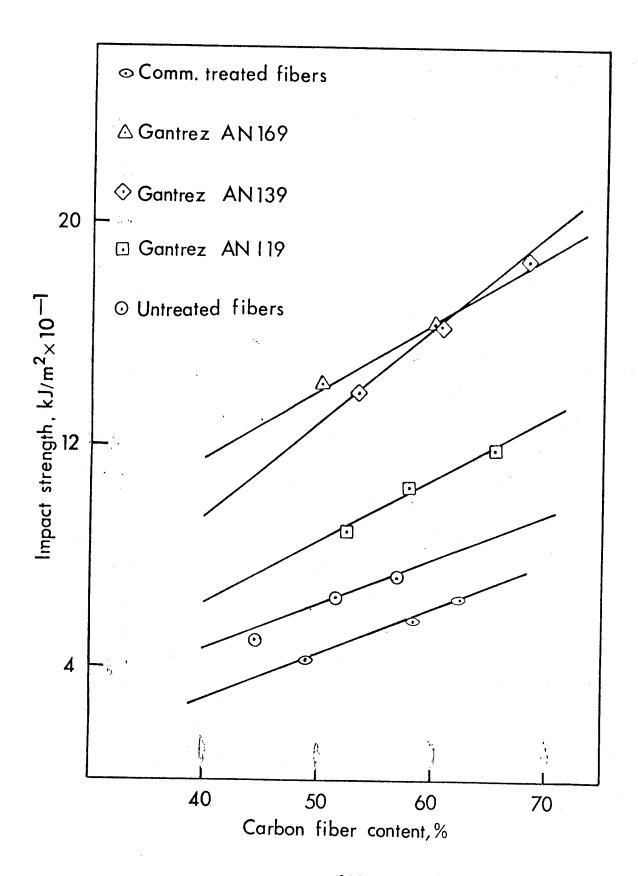


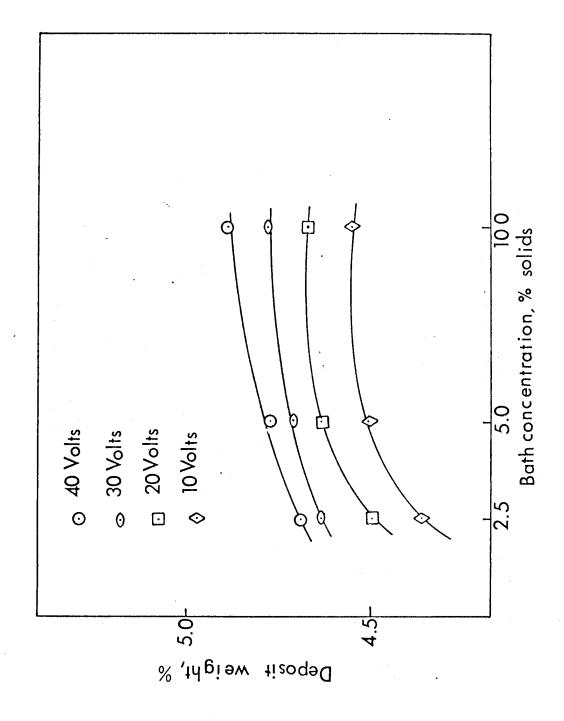
Interlaminar Shear of Composites Prepared from Fibers Coated with (a) Acrylic Acid (b) PFAZ 300 (c) DAA 2.5 seconds (d) Styrene (e) MMA (f) Styrene/Acrylonitrile (g) ϵ -Caprolactam (h) EPON 828/Phthalic Anhydride (i) VTBN (j) and Untreated Hercules AU Carbon Fiber

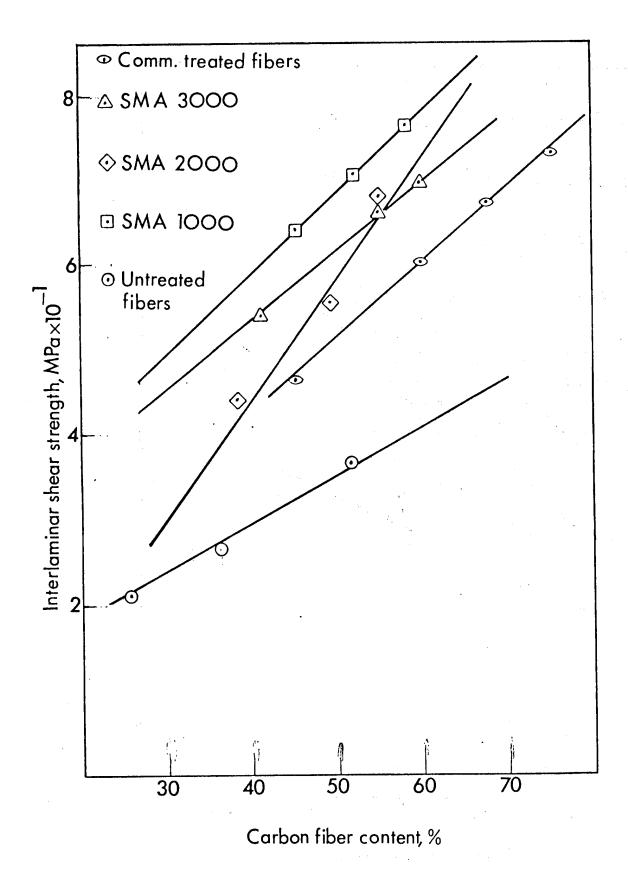


Impact Strength of Composites Prepared from Fibers Coated with (a) PFAZ 300 (b) DAA 10 Seconds (c) DAA 2.5 Seconds (d) Hercules Au and (e) Hercules AS Carbon Fiber

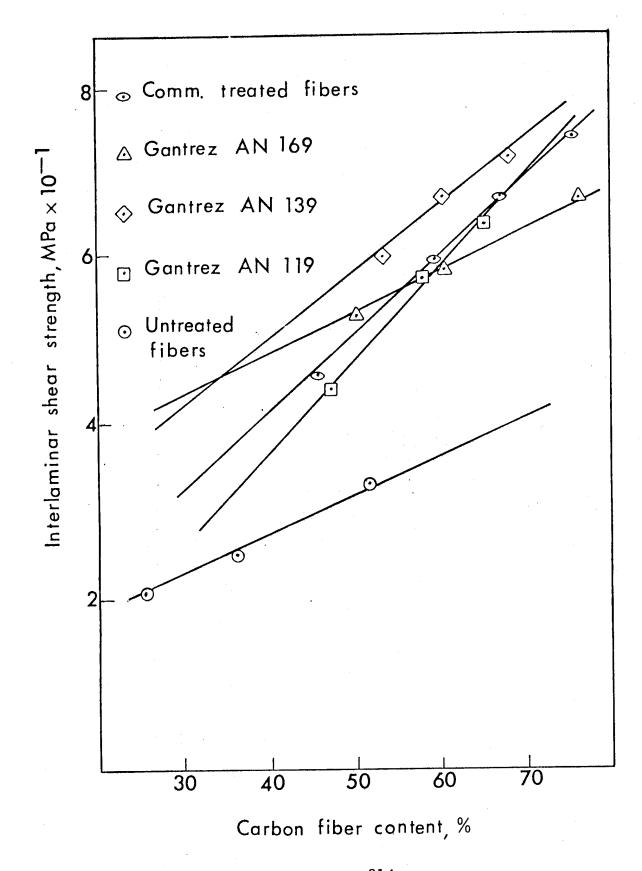
Subranian







213



SOME DEAS AND PREIMINARY RESULS TO STEVATE RECTRICAL PROBLEMS OF CARBOY FIDER CONFOSTES

Kumar Ramohalli

WARREN DOWLER, ROBERT GAULDIN, JOHN QUINN, FRED TERVET DONALD UDLOCK, GIULIO VARSI, LIEN YANG



SOLID PROPULSION AND ENVIRONMENTAL SYSTEMS SECTION JET PROPULSION LABORATORY PASADENA, CALIFORNIA

WORKSHOP ON CARBON FIBERS, N.A.S.A. LANGLEY RESEARCH CENTER HAMPION, VIRGINIA 23, 24 MARCH 1978

INTRODUCTION



 CARBON FIBER COMPOSITES HAVE RELEASED FIBERS WHEN BURNED WITH AGITATION

NASA TM 78652 DOC NEWS ITA-78-13 TIME 13 MARCH

FIBERS HAVE CAUSED ELECTRICAL PROBLEMS

ULTIMATE AIM: PREVENT RELEASE OF CONDUCTING FIBERS

IMMEDIATE AIM: GENERATE IDEAS AND RESULTS SHOWING PROMISE

THIS PRESENTATION

BASIC IDEAS

• TEST METHODS

■ EXPERIMENTAL RESULTS

SUMMARY AND FUTURE WORK

BASIC APPROACH



PREVENT RELEASE OF CONDUCTING FIBERS

BEFORE USE IN RESIN

COAT FIBERS WITH DIELECTRIC

COAT FIBERS WITH CATALYST FOR GASIFICATION (C, CO, CO2)

COAT FIBERS WITH CHEMICALS TO HOLD THEM IN MATRIX (CROSSLINK, CHAR)

TEST METHODS

● AROUND A BURNING COMPOSITE, FOR SPECIFIED TIME

COUNT NUMBER OF FIBERS

COUNT NUMBER OF SHORTS IN TYPICAL CIRCUIT

EXPERIMENTS

• BURN TESTS, TGA STUDIES, SEM, EDAX DATA

• TEST CIRCUITS

CATALYSIS



SODIUM IS SHOWN TO CATALYSE GASIFICATION (REF WENDT et. al.)

SMALL AMOUNTS ON FIBER

SHOULD NOT AFFECT SERVICE LIFE

CANDIDATES SO FAR:

• NaNO₃, LinO₃, KMnO₄, PPQ, FeAA, COBALT NAPHTHENATE

■ TGA STUDIES:

IN AIR AND NITROGEN (ALSO ARGON AS A CHECK IN FEW CASES)
 THORNEL-300 (PLAIN, AND COATED BY DIP IN SOLUTION)
 20°C/MIN TO 1000°C

REPRODUCIBILITY CHECKED (5% MAXIMUM ERROR)

PPQ APPEARS PROMISING ON THORNEL-300 (IN AIR)

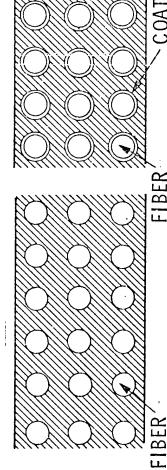
PLAIN COATED WITH PPQ 100 AT 665°C WEIGHT LOSS PERCENT ● TEMPERATURE °C 550 600 650 700



PREVENTION OF RELEASE FROM MATRIX

BASIC IDEA

COAT FIBER WITH CHEMICALS THAT DEGRADE AT SURFACE TEMPERATURE OF BURNING COMPOSITE



TYPICALLY COAT IS 2% - 5% OF TOTAL WEIGHT

STATE-OF-THE-ART COMPOSITE

COATED FILLER COMPOSITE

- SIMILAR IDEA WORKED WELL IN ANOTHER COMPOSITE SYSTEM (REF. WSS/CI 77-16)
- 1. (95% ETHYL CELLULOSE + 5% TRICRESYL PHOSPHATE) 2. COBALT NAPHTENATE

CANDIDATE CHEMICALS:

- 3. SODIUM SILICATE
- COMPOSITES PREPARED IN

■ EPOXY (80% RF-3000 + 20% RF-61) | MOST OF THE TESTS

POLY IMIDE (NR-150)

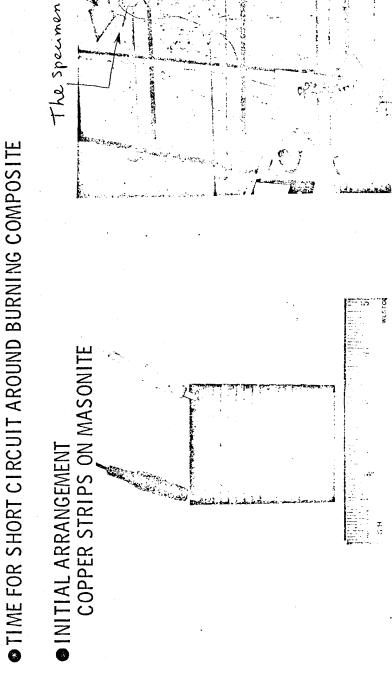
AIMED AT 30% RESIN AND 70% FIBERS

TESTS NEEDED FOR PROOF OF CONCEPT

HOURS LESS TO SELECTION OF THE SELECTION

est circuit board

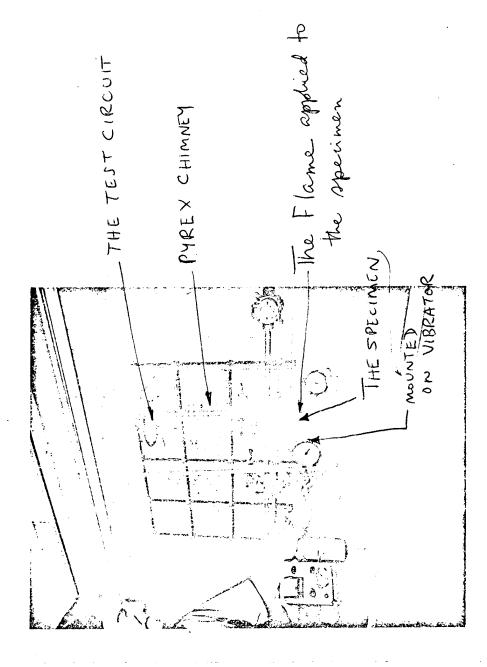




PROBLEMS WITH BOARD GAVE SHORTS WITH RESIN ALONE

IMPROVED DESIGN

PRESENT ARRANGEMENT





RESCH IS

INITIAL BOARD DESIGN (TIME FOR SHORT)

COATED WITH ECTTCP	. 22	. 21	22.	12	22	. 18	19	21	21
PLAIN	55	15	5	12	15	. 10	10	20	14

PRESENT SET UP

COATED WITH ECTTCP	18 SEC
PLAIN	12 SEC

• PRELIMINARY TESTS WITH SODIUM SILICATE AS THE COAT:

- NO SHORTS IN WELL OVER A MINUTE
 - THE COAT CONTENT WAS ABOUT 20%
- TESTS UNDERWAY TO HAVE SMALL COAT CONTENT





THE LATEST RESULTS

SODIUM SILICATE APPEARS VERY PROMISING

WEIGHT PERCENT COATING IS CAREFULLY CONTROLLED

• 2%, 5%,

6.93%, 12%,

19.06%

ALL OF THEM ARE CAST IN EPOXY (40%/60%-FIBERS/EPOXY)

BURNED IN STANDARD SETUP

THE 2% COATED SAMPLES GAVE NO SHORTS AT ALL (>90 SECS)

RESIN BURNED OFF IN 7 SECONDS

FIBERS FELL DOWN IN BUNDLES

WILL BE PURSUED IN DETAIL

SUMMARY AND FUTURE PLANS



PROBLEM RECOGNIZED

THREE TASKS

CATALYZE GASIFICATION
 PPQ SHOWS PROMISE

 PREVENT RELEASE FROM RESIN CHAR EC+TCP SHOWS PROMISE SODIUM SILICATE LOOKS VERY GOOD

CIRCUIT BOARD APPEARS ADEQUATE FOR RANKING DEVELOP TEST METHODS

FUTURE

CONTROL COAT CONTENT AND RESIN CONTENT

MORE TESTS (IN NBS SMOKE DENSITY CHAMBER ALSO)

MECHANICAL PROPERTIES

AGING STUDIES (SERVICE LIFE)

THERMOCHEMICAL MODEL

EPOXY RESIN MODIFICATIONS Dr. James Noland, Chairman

NAME

John Parker

Walter S. Cremens

ORGANIZATION

Norman B. Sunshine Narmco Materials Inc. David Crabtree Northrop Aircraft Co. Shell Development Co. C. V. Wittenwyler U.S. Polymeric (Div. of HITCO) Sidney W. Street Richard J. Moulton HEXCEL M. J. Katsumoto Boeing Commercial Airplane, Co. Robert A. Frigstad 3-M Co. AFML/MBC C. E. Browning James D. Allen Fiberite Corp. James Noland American Cyanamid Co. Clayton May Lockheed M&S Mal Katsumoto Boeing C/AC R. J. Tomerlin Bell Helicopter William A. Mueller JPL R. C. Curley McDonnell Douglas R. E. Hoffman Hercules Inc. Marvin Rhodes NASA Larc

NASA Reporters: Paul Hergenrother, Norman Johnston, LaRC

Lockheed-Georgia

NASA Ames

ISSUES FOR

EPOXY RESIN MODIFICATIONS

WORKING GROUP

- 1. What is the most important new resin property that must be designed into any modified epoxy?
- 2. Can char formers be mixed into an epoxy matrix and still be effective?
- 3. For each epoxy modification considered:
 - (a) What is the minimum modification that will retard fiber release?
 - (b) Are current snythetic and fabrication processes applicable to the modified epoxy?
 - (c) Will this modification be cost effective?
 - (d) How soon can the modification be made and produced in large quantity for the aerospace industry?
 - (e) Will this modification possess the environmental durability of current epoxy?
 - (f) Will the data base already in hand with current graphite-epoxy composites have to be regenerated using this modified material? If so, how much would have to be regenerated?
 - (g) What is the main principle that the modification uses to retard graphite fiber release?
 - 4. What is your assessment of the current NASA research program in this area, and what changes do you recommend?
- 5. Rank the different generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS' SUMMARY FOR EPOXY RESIN MODIFICATIONS WORKING GROUP

Proposed solutions involving epoxy resin modification were divided into two categories: short-term approaches and long-term approaches. The prepreggers and fabricators adamantly opposed any change to the resin or reinforcement since such modifications would require complete resin and composite requalification. The group also felt that any fix must impose a minimum weight penalty on the composite structure. Since the primary driving force for the use of graphite composite in place of the more conventional material (Al) is a 20 percent weight savings, they felt that this advantage should not be compromised.

Short-term Solutions. Proposed short-term solutions were restricted to changes that did not involve alteration of the chemical structure or chemical content of the matrix. The group proposed the use of an outer coat of an intumescent point and/or a ply (plies) of flame retardant intumescent resin. However, the group felt that an outer intumescent surface would be unlikely to restrict the release of fibers since the char foam formed by intumescent materials is weak and friable.

Long-term Solutions. - Proposed long-term solutions included the use of flame retardant additives such as red phosphorus, phosphate compounds, aluminum hydroxide, subliming salts and trimethoxy boroxine. Unfortunately, each additive introduces its own peculiar problem such as the difficulty of obtaining and handling red phosphorus of small particle size (e.g., 1 µm), the weight penalty associated with the use of aluminum hydroxide, and the moisture problem anticipated with the use of trimethoxy boroxine. Brominated epoxy resins were also proposed, but their poor char-forming characteristics and increased weight make them unattractive. Also, blends of epoxy resins with high char-forming non-epoxy resins such as bis-maleiimides and phenolics were proposed. No changes in epoxy resin chemistry were suggested.

CONCLUSIONS

1. The present momentum in the development of graphite reinforced composites must be maintained. Any delay would severely impact the development and near-future use of these materials.

2. There is no "quick-fix" or short-term solution to the problem through modification of the epoxy matrix. The prepreggers, especially, indicated that the chemistry of epoxy resins does not permit a modification that would resolve the problem while maintaining all of the required features of a graphite-epoxy prepreg (e.g., low cost, tack and drape, shelf-life, autoclave cure at 350 F, etc.). In addition, the group complained that a lack of information existed to indicate what epoxy alterations, if any, (e.g., increased char formation) would alleviate the problem.

RECOMMENDATIONS

- l. Insufficient manpower was proposed to conduct the resin modification work as proposed. Therefore, the group recommended that NASA increase its manpower loadings in this activity.
- 2. Inorganic coatings on graphite fiber were considered to be long-term high risk solutions. Insurmountable problems due to coefficient of thermal expansion mismatch resulting in a weak interface area and problems due to poor adhesion to epoxy resins, brittleness of the coating, and moisture sensitivity were anticipated from the use of inorganic coatings.
- 3. The most promising short-term solutions need more emphasis.
- 4. The risk analysis work should be completed as soon as possible and faster than the current proposed schedule (1.5 years).
- 5. A published schedule of NASA decision points such as dates for completion of the risk analysis and development of standardized tests is urgently needed.

REPORT OF

EPOXY RESIN MODIFICATIONS WORKING GROUP

DR. JAMES NOLAND, CHAIRMAN

EPOXY RESIN MODIFICATION

OVERVIEW

MOMENTIM	
PRESENT	֝֝֝֝֝֝֝֝֝֝֝֜֜֜֝֝֝֡֜֜֜֝֝֡֜֜֜֝֡֓֜֜֜֜֝֡֓֜֜֜֜֡֡֜֜֜֜֡֡֜֜֜֡֡֡֡֜֜֡֡֡֡֡֜֜֡֡֡֡֡֡֡֡
ANCE OF	֓֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜֜
MAINTENANCE	
C	,

O NO MODIFICATION OF EPOXY AS SHORT-TERM SOLUTION

O RISK ANALYSIS NEEDS FASTER PACE

o PUBLISHED SCHEDULE FOR DECISION - POINTS NEEDED

SHORT-TERM SOLUTIONS

- CHANGE IN EPOXY RESIN REQUIRES TOTAL REQUALIFICATION 0
- ALL SHORT-TERM SOLUTIONS INVOLVE NON-STRUCTURAL MODIFICATIONS 0
- O INTUMESCENT PAINT
- OUTER PLIES OF FLAME-RETARDANT INTUMESCENT RESIN 0
- NO-WEIGHT OR MINIMUM-WEIGHT PENALTY

0

LONG-TERM SOLUTIONS

-EPOXY RESIN MODIFICATION-

- O IMPROVED FIRE RESISTANT ADDITIVES
- RED PHOSPHOROUS AND PHOSPHORUS COMPOUNDS
- O ALUMINUM HYDROXIDE
- o SUBLIMING SALTS
- o ENCAPSULATED TRIMETHOXY BOROXINE
- O BROMINATED EPOXY RESINS (UNLIKELY SOLUTION)
- -CHANGES IN RESIN CHEMISTRY-
- o PHENOLIC CURES
- O BIS-MALEIMIDE BLENDS
- O OTHERS!

RANKING OF LONG-TERM SOLUTIONS

RIORITY

EPOXY REPLACEMENTS	FIBER COATINGS (ORGANIC)	HYBRIDS
I EP(2 FII	3 HYE

EPOXY MODIFICATIONS

RECOMMENDATIONS

SCOPE OF RESIN MODIFICATIONS TOO BROAD FOR MANPOWER 0

LOADINGS: RECOMMEND INCREASED MANPOWER

INORGANIC FIBER COATINGS ARE LONG-TERM, HIGH RISK 0

SOLUTIONS

O SHORT-TERM SOLUTIONS NEED MORE EMPHASIS

O NASA ROADMAP URGENTLY NEEDED

EPOXY RESIN REPLACEMENTS Dr. B. F. Landrum, Chairman

NAME

ORGANIZATION

Composites Horizons Ira Petker Naval Research Lab Lynn Jarvis Acurex/Aerotherm Chad Delano United Technologies Res. Ctr. Dan Scola Lockheed-California W. F. Baumgartner Hughes Aircraft Co. Norm Bilow McDonnell Douglas Henry M. Toellner Lockheed-Georgia Walter S. Cremens Hexcel Rick Moulton Don Houston Rockwell - Space Jim Gauchel DeSoto Inc. U. of Maryland William J. Bailey NASA Ames John Parker Ronald Stocks CIA OSI/LSD Rex Gosnell Riggs Engineering General Dynamics/Convair Ed Harrison General Dynamics/Conair Vance Chase William Verzino Aerospace Corp. Mike O'Rell TRW Systems John T. Hoggatt Boeing Aerospace Hugh H. Gibbs DuPont Ciba-Geigy Corporation Bill Landrum NASA Larc George Sykes

NASA Reporter - Dr. Terry St. Clair, LaRC

ISSUES FOR

· EPOXY RESIN REPLACEMENTS

WORKING GROUP

- 1. What principles would be employed by replacement resins to retard fiber release?
- What combination of properties must a resin possess in order to replace epoxy and at the same time retard fiber release?
- 3. Are aromatic polyimides a good candidate resin system to replace epoxy for the purpose of retarding fiber release?
- 4. For each epoxy replacement resin proposed:
 - (a) Are current synthetic and fabrication processes applicable to the new resin? Could improved processes be developed?
 - (b) Will this new resin be cost effective?
 - (c) Will this new resin possess the environmental durability of current epoxy?
 - (d) What is the main principle that this new resin would employ to retard fiber release?
 - (e) How soon can this new resin be produced in large quantity for the aerospace industry?
- 4. What is your assessment of the current NASA research program in your area, and what changes do you recommend?
- 5. Rank the generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS SUMMARY FOR EPOXY RESIN REPLACEMENTS WORKING GROUP

The meeting was prefaced with four presentations which are summarized below.

- 1. Lynn Jarvis (NRL) This was a summary of NRL work on polyphthalocyanine (PPCy). The polymer is a high char former, is made from a single monomer, has a high degree of toughness, and may be available for as little as \$10/1b within 2 years. NRL is still modifying the chemistry of the system. The current versions have a 410-490°F cure and afford a dry, boardy prepreg. Very little data base exists for the PPCy. The group consensus was that this material needs further development before commercial applications could be realized.
- 2. Bill Bailey (U. of Maryland) This was a presentation on the need for epoxy replacements to have low shrinkage. He feels that low shrinkage will minimize microcracking which promotes resin burnout. He also feels that lower shrinkage will cause better resin-to-fiber adhesion which would help hold the fibers together in a fire/explosion scenario. He presented the chemistry of a material he has developed which has applications as a dental adhesive because of its low shrinkage. The resin did not have the high temperature capability of 350°F cure epoxies.
- 3. Mel Katsumoto (Boeing) This was a summary of the problems a commercial airplane builder faces in qualifying a resin for use on aircraft. He charged the group to look for a "quick fix," such as a composite protective coating, to solve the current fiber release problem, then formulate a long-term program to develop an epoxy replacement resin.
- 4. Raymond Kray (Ciba-Geigy) This was a summary of some of the NCNS resin work performed on contract to NASA-Langley. Data were shown on NCNS's excellent resistance to burning, and the slight intumescent behavior of NCNS/graphite laminates was described. NCNS is not commercially available, at present, but may be in approximately one year. The resin is projected to cost about \$5-\$8/lb.

In response to the strawman issues posed by NASA to the group, a list was compiled of the properties that an effective epoxy replacement resin should possess.

1. It should have a high char yield and produce a tough char.

- 2. It should be intumescent.
- 3. It should have mechanical properties equal to those of the current epoxies.
- 4. It should have a high limiting oxygen index (LOI).
- 5. Its properties should match ignition and burn properties of the fiber.
- 6. It should be UV resistant.
- 7. It should meet processing requirements of current epoxies.
- 8. It should present no unacceptable toxic on environmental hazard.
- 9. It should be moisture stable.
- 10. It should sell for \$10/1b or less.
- ll. It should have a maximum cure temperature of $350^{\circ}F$ and preferably lower.

In response to the chairman's request for potential epoxy replacement resins from currently available materials, the following list of possible candidates was compiled:

1. Polyimides and Cyanates

LaRC 160
PMR-15 (First and Second Generation)
NR-150 A2
Thermid 600
Hexcel F-178
N-Cyanosulfonamide (NCNS)
Triazine A

2. Phenolics and Miscellaneous

Weyerhauser benzyl resin
Phenolic prepregs from Ciba-Geigy, Fiberite,
Hitco, and Narmco
Polyphthalocyanines (PPCy)
Polyphenylene sulfides
Aryl sulfones
Thermally cross-linked thermoplastics

CONCLUSIONS

- 1. For a short term solution, only existing resin systems should be considered as replacements for epoxy.
- 2. Toughness is an important property to be considered in evaluating potential replacement resins.
- 3. Hybrid composites and/or fiber coating concepts offer the best hope for a "quick fix" to the graphite fiber hazard. Fiber modification is the least promising approach.

RECOMMENDATIONS

- 1. NASA should conduct a screening test program on existing replacement resins to characterize their burn properties and identify promising candidates. Selection of systems for further research should be based on fabrication parameters such as prepreggability, handleability, and processability into laminates and on mechanical properties of composites.
- 2. NASA should appoint an Epoxy Replacement Panel that should meet every six months to review and discuss progress.

REPORT OF

EPOXY RESIN REPLACEMENTS WORKING GROUP

DR. B. F. LANDRUM, CHAIRMAN

EPOXY RESIN REPLACEMENTS

OVERVIEW

PRINCIPLES TO BE EMPLOYED

CRITICAL PROPERTIES

PROMISING KNOWN SYSTEMS

PROBABILITY OF SUCCESS

ASSESSMENT OF CURRENT NASA PROGRAM

DESIRED RESIN CHARACTERISTICS

A NEW RESIN TO BE AN EFFECTIVE EPOXY REPLACEMENT MUST EMPLOY AS MANY OF THE FOLLOWING PRINCIPLES AS POSSIBLE

- HIGH CHAR FORMATION
- O INTUMESCENT
- HIGH LIMITING OXYGEN INDEX
- MATCH IGNITION & BURN CHARACTERISTICS OF FIBER
- D PRODUCE TOUGH CHAR WITH GOOD FIBER ADHESION
- O EXHIBIT ACCEPTABLE PROCESSING CHARACTERISTICS
- O DEMONSTRATE EPOXY MECHANICAL PROPERTIES
 - SELL FOR \$10,00/LB OR LESS
- PRESENT NO UNACCEPTABLE TOXIC OR ENVIRONMENTAL HAZARD IN PROCESSING

CONSENSUS CONCLUSION

RANKED IN ORDER OF PROMISE DUE TO LACK OF A SYSTEMATIC SCREENING CURRENTLY AVAILABLE, WELL KNOWN RESIN SYSTEMS CANNOT BE STUDY BY A CENTRAL CLEARING HOUSE OR AUTHORITY,

RECOMMENDATION:

NASA ESTABLISH A SET OF STANDARD EVALUATION PROCEDURES AGAINST WHICH CANDIDATE RESIN PROPERTIES WILL BE DETERMINED.

POLYIMIDES & CYANATES

LaRC 160

PMR - 15 (1st.& 2nd GENERATION)

NR - 150 A2

THERMID 600

F - 178

NCNS .

TRIAZINE A

PHENOLICS & MISCELLANEOUS

XYLOK

WEYERHAUSER BENZYL RESINS

PHENOLIC PREPREG -

NARMCO

FIBERITE CIBA-GEIGY

HITC0

POLYPHTHALOCYANINES

THERMOPLASTICS

POLYPHENYLENE SULFIDES

ARYL SULFONES THERMALLY CROSS LINKED THERMOPLASTICS

CURRENT NASA PROGRAM ASSESSMENT

- o GOOD START
- O NEED OPEN SCREENING OF AVAILABLE RESINS
- NEED BETTER DEFINITION OF REALISTIC SCREENING CRITERIA. 0
- EFFORTS SHOULD BE CONCENTRATED ON DEVELOPING 3 OR 4 MOST PROMISING SYSTEMS, 0
- NEED EARLY FEEDBACK FROM PREPREGGERS AND FABRICATORS 0

SUMMARY OF RECOMMENDATIONS

- SCREEN KNOWN RESIN SYSTEMS AGAINST A SET OF STANDARD CRITERIA 0
- O SELECT MOST PROMISING CANDIDATES ABOVE FOR FURTHER EVALUATION
- COMPARE COST/PERFORMANCE AND SELECT MOST PROMISING FOR FULL SCALE DEVELOPMENT 0
- WASA SHOULD REQUEST DATA FROM RESIN PRODUCERS CONCERNING PERTINENT RESIN PROPERTIES 0
- UNDERTAKE SELECTIVE SYNTHETIC MODIFICATIONS TO EXISTING RESIN SYSTEMS 0
- ESTABLISH INDUSTRY/GOVERNMENT/UNIVERSITY REVIEW BOARD TO ASSESS PROGRESS 0

NRL WORK ON POLYPHTHALCYANINE

LYNN JARVIN NRL

MARCH 23, 1978

Navy

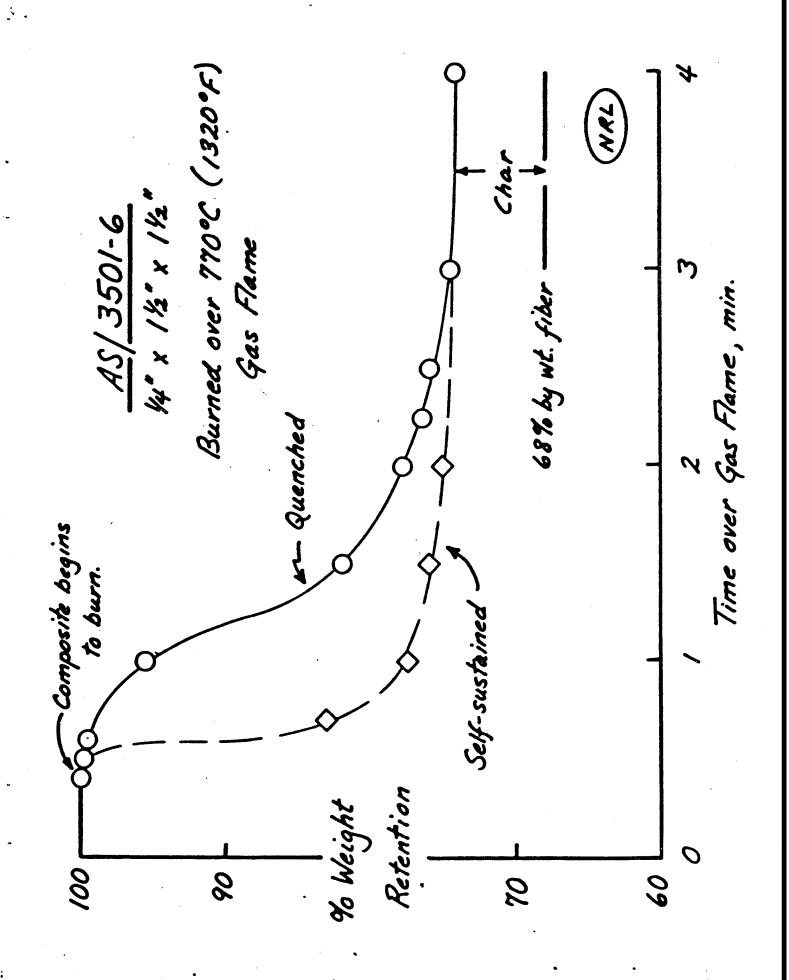
POLYMERIZATION REACTION

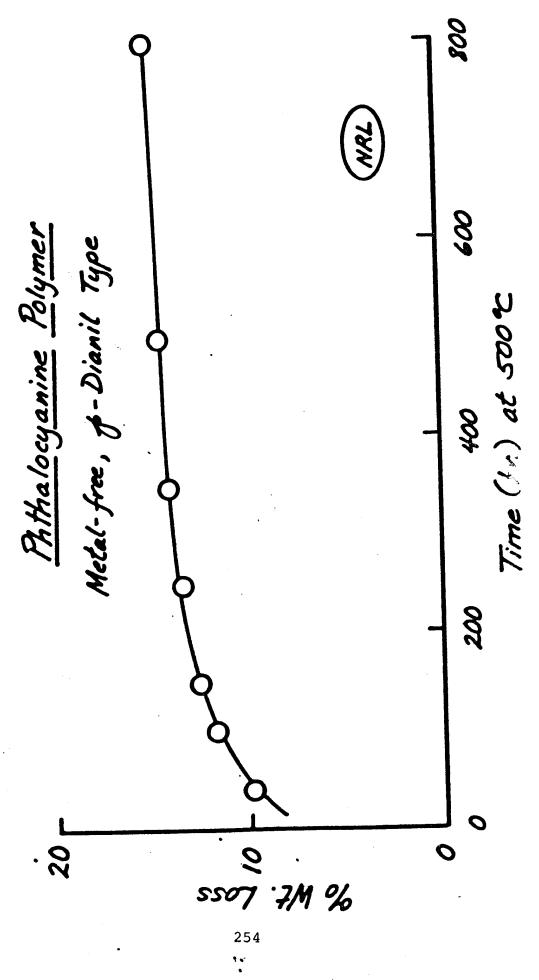
POSSIBLE RESEARCH DIRECTIONS

- \bullet May increase char yield by: addition of aromatic groups to R addition of suitable metal atoms (Sn_1--)
- Modify synthesis to REDUCE COST
- . Maintain properties as matrix material

ADVANTAGES OF POLYPHTHALOCYANINES

- . ONE PHASE SYSTEM
- . INFINITE SHELF LIFE
- POTENTIAL LOW COST (~ \$10/LB)
- EASILY PROCESSED
- . No volatiles on curing (no voids)
- . HIGH CHAR YIELD POSSIBLE

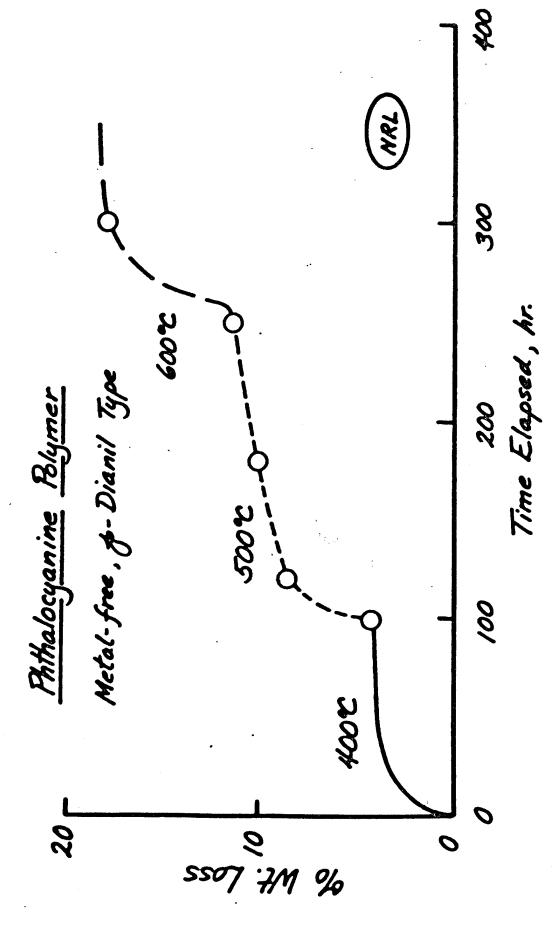




Composites from 170°C Gas Fire

Char/Fiber, Appearance Wt. ratio after Burning	0.28 Completely	0.29 delaminated	0.17 Solid block	0.14 Partially delaminated
% Char C Yield	9 61	6/	#3	65
Resin Type	Hercules epoxy	Narmeo epoxy	Hexcel polyimide	NRL poly- phthalocyanine
Composite	9-1255/SV	7300/5208	T300/ F178	T300/C-10

(NRL)



NCNS RESINS

RAY KRAY

CIBA-GEIGY

MARCH 23, 1978

COMPOSITION AND CURING MECHANISM

OF N-CYANOSULFONAMIDE LAMINATING RESIN

NCNS-13P RESIN PILOT PLANT BATCH NO. 7/7/1002

LAMINATING VARNISH I-25R-99

REINFORCEMENT

B-STAGING CONDITIONS FOR PREPREG

NO. OF PLIES

PRESS LAMINATION CONDITIONS

POST CURE CONDITIONS

RESIN SOLIDS CONTENT

FIBER VOLUME

VOID CONTENT

400°F SHORT BEAM SHEAR STRENGTH, PSI

400°F FLEXURAL STRENGTH, PSI

400°F FLEXURAL MODULUS, KSI

30% NCNS-13P IN 60/40 METHANOL/ETHYL ACETATE

UNIDIRECTIONAL AS GRAPHITE FIBER 70°C/75 MIN. - 85°C/15 MIN.

15

350°F/300 PSI/1 HR.

425°F/7 HRS. - 460°F/8 HRS.

30.3%

64.8%

NONE

11,400

237,000

17,200

TMA Z-AXIS THERMAL EXPANSION

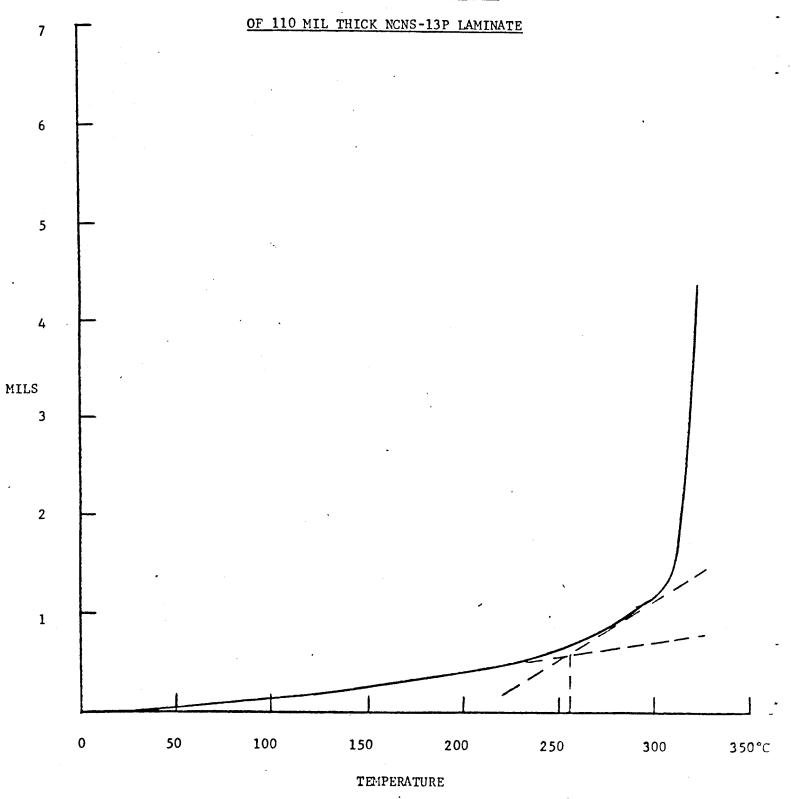


FIGURE 14

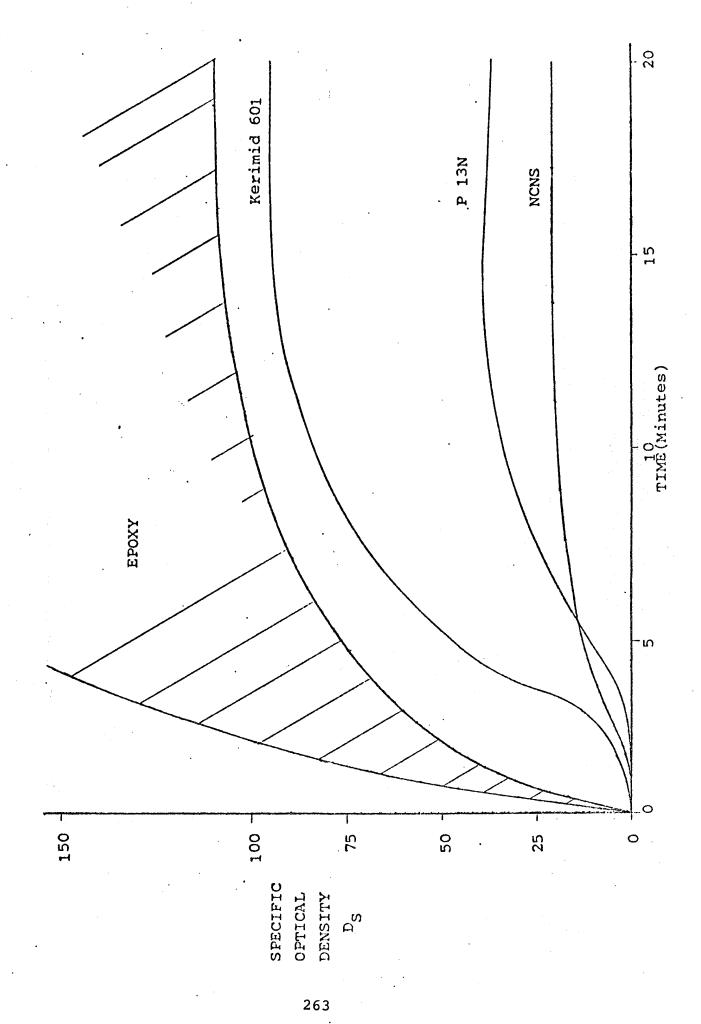
AMMABILITY AND SMOKE GENERATION

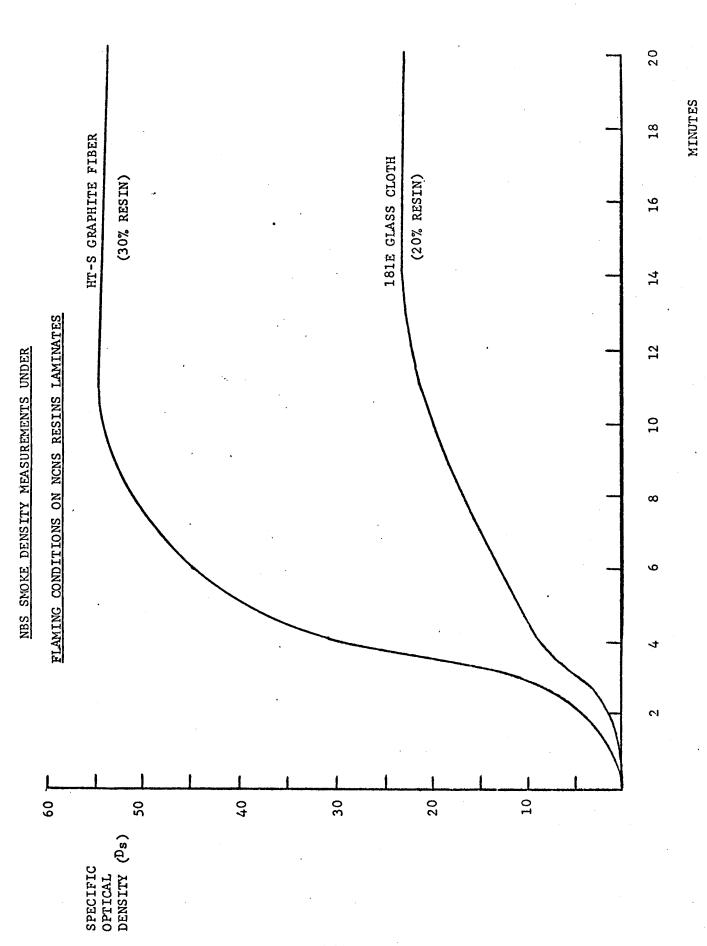
	1:2 NCNS RESIN	P13N RESIN	XYLOK 210
OXYGEN INDEX OF NEAT RESIN	29	31	;
RESIN CONTENT OF 181E GLASS LAMINATE	30	27	30
OXYGEN INDEX OF LAMINATE	86.2	!	69
MAXIMUM SPECIFIC OPTICAL DENSITY (DM) FLAMING NON-FLAMING	20 6	20 0.3	123
TIME IN MINUTES TO DEVELOP SPECIFIC OPTICAL DENSITY = 16 (DS) FLAMING NON-FLAMING	6.6 NOT REACHED	7.5 NOT REACHED	1.8

NON-BURNING CHARACTERISTICS OF NCNS/181E GLASS CLOTH LAMINATES

NO. 95 RESIN NCNS-12M RESIN CONTENT 22.8% FAA VERTICAL BURN TEST 25.853A* FLAME TIME IN SECONDS 6.2 BURN LENGTH IN INCHES 1.1 LIMITING NON-BURNING OXYGEN IN 100% 02 INDEX (LOI)

^{*}ALL SAMPLES WERE SELF EXTINGUISHING AND DID NOT DRIP.





TOXIC GASES FROM NCNS-13P/181E GLASS FABRIC LAMINATE I-24A-119A IN NBS SMOKE DENSITY CHAMBER

D _M		12		
TIME IN MINUTES	5	10	15	20
CO, PPM	10	30	70	110
HCN, PPM	1*	2	3.5	5
SO ₂ , PPM	2.5	,5	5	5
NOX, PPM	0.5	1	2	2

^{*}COMPARATIVE VALUE FOR POLYIMIDE 3002 (DUPONT) WAS 15 PPM FOR HCN (D. ARNOLD & G. JOHNSON, BOEING, SAMPE SYMPOSIUM APRIL 1977).

LOW SHRINKAGE RESINS

BILL BAILEY UNIVERSITY OF MARYLAND

MARCH 23, 1978

		6	Ç.
MONOMER	SPECIFIC GRAVITY	GRAVITY	SHRINKAGE
	MONOMER	POLYMER	%
VINYL CHLORIDE	0.919	1.406	34
ACRYLONITRILE	0.797	1.17	31

METHYL METHACRYLATE 0.940

267

0.932

VINYL ACETATE

<u>..</u>

7

STYRENE

DIALLYL PHTHALATE

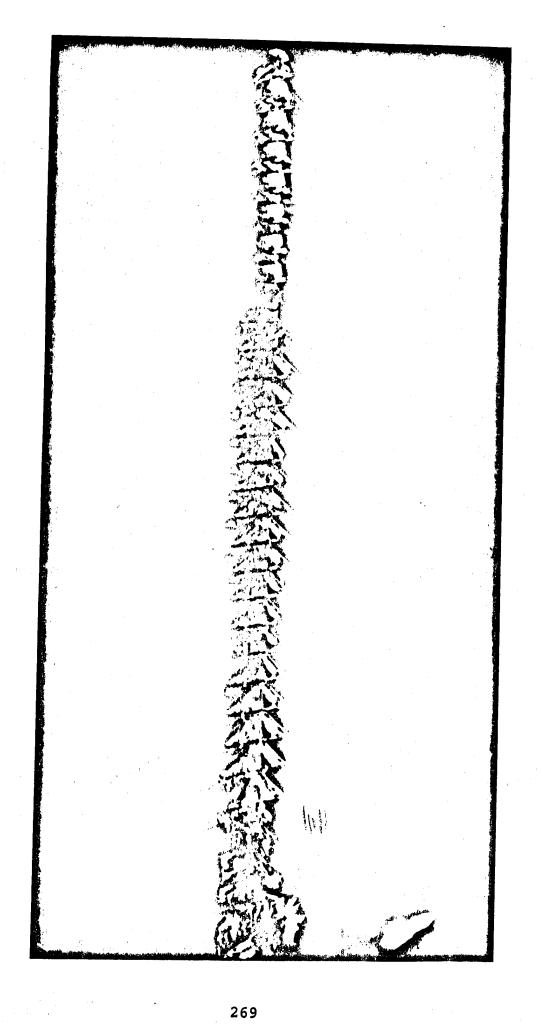
0.907

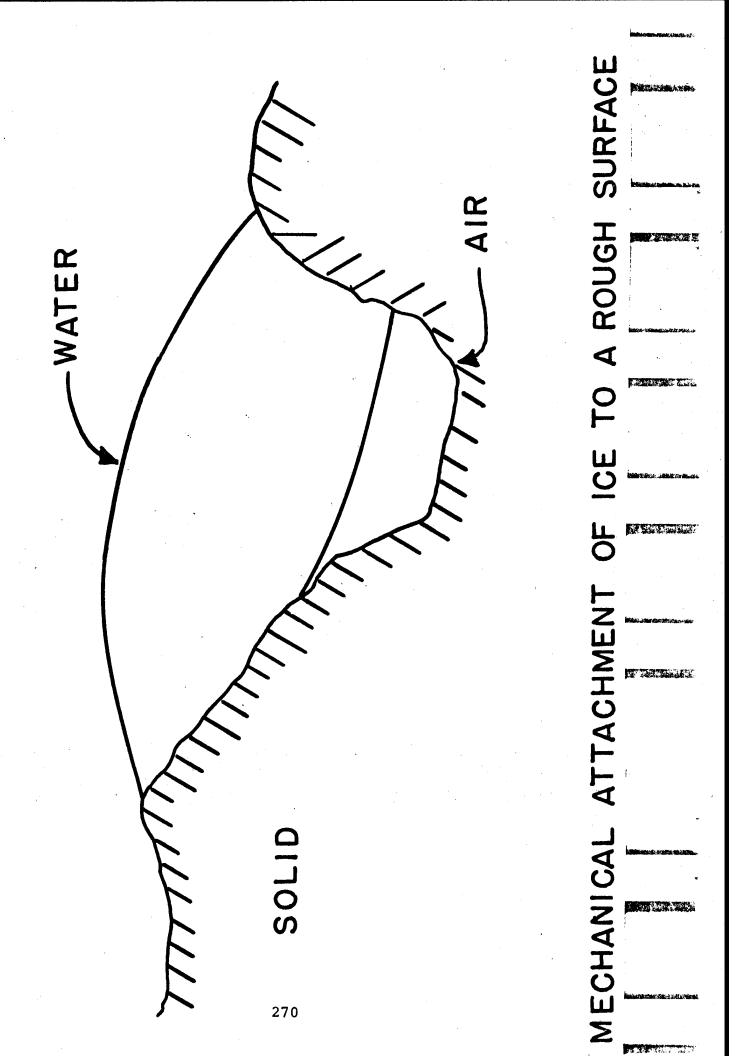
90.1

1.27

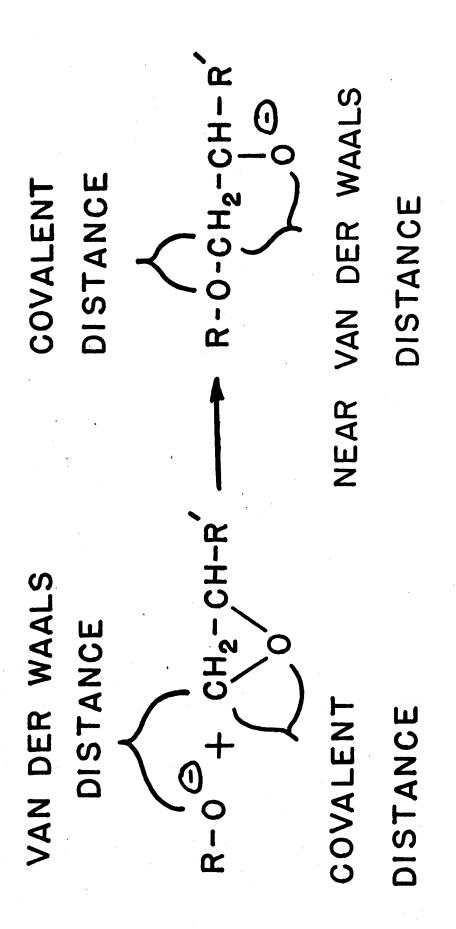
POLYMERIZATION SHRINKAGE DURING RING-OPENING

MONOMER	d ²⁰	POLYMER 420	d4 SHRINKAGE,%
ETHYLENE OXIDE	0.869	8	23
	0.830	1.002	
	0.772	5	
STYRENE OXIDE	0		O
CYCLOOCTENE	0.849	0.89	ហ
CYCLODODECATRIENE	0.885	0.91	m

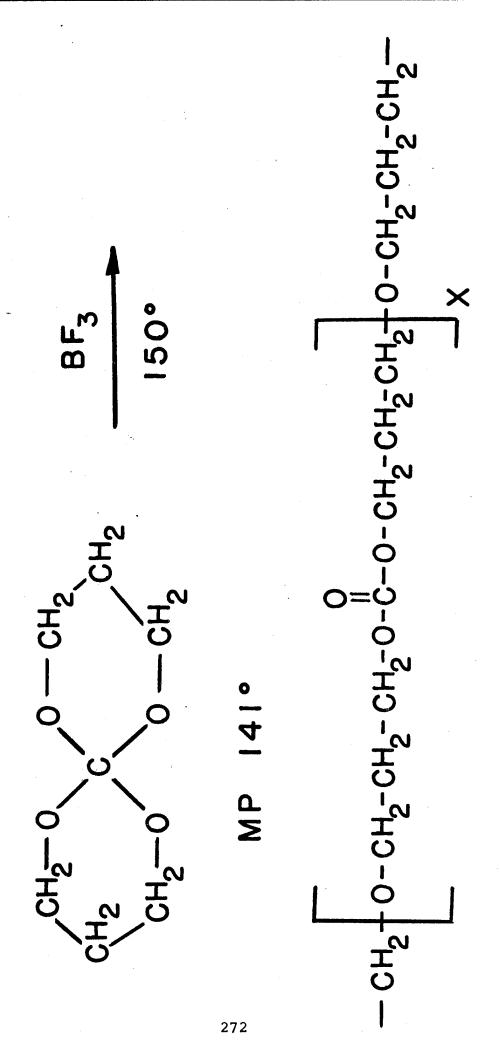


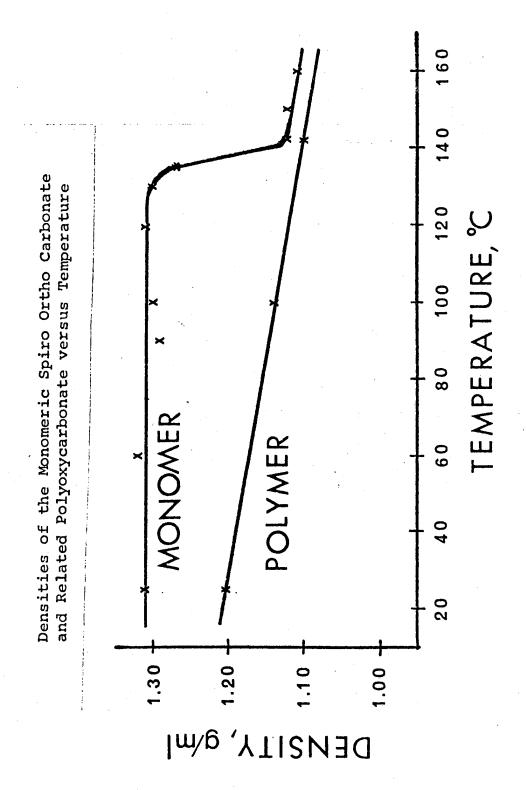


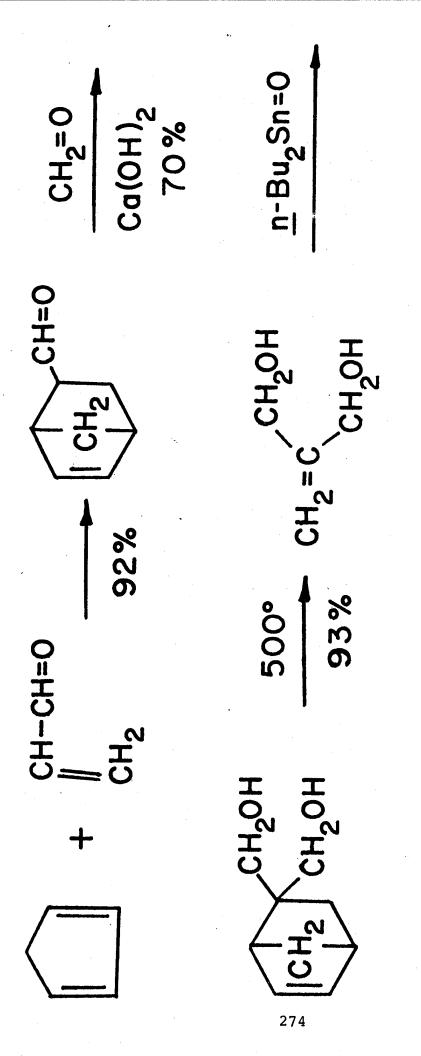
POLYMERIZATION RING-OPENING SHRINKAGE DURING

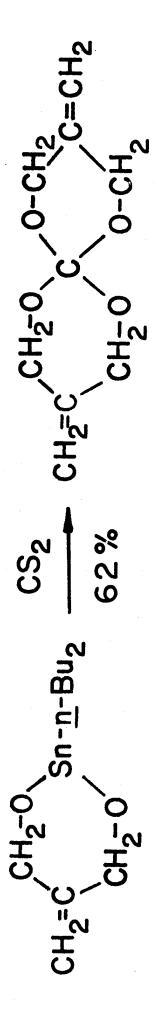


3-5% SHRINKAGE





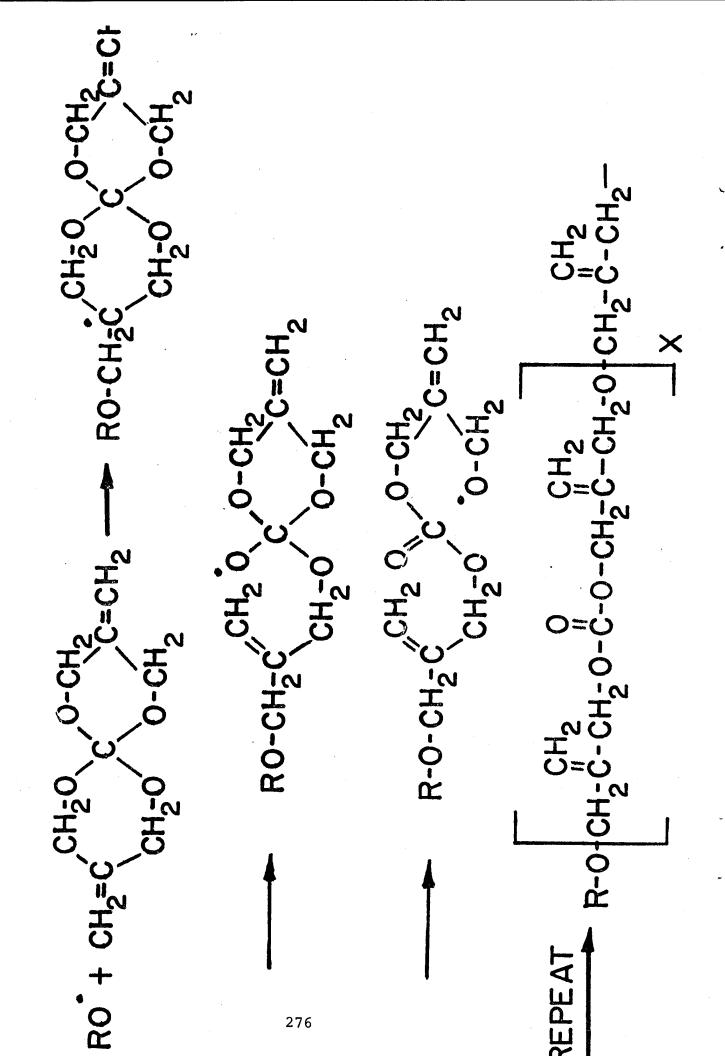


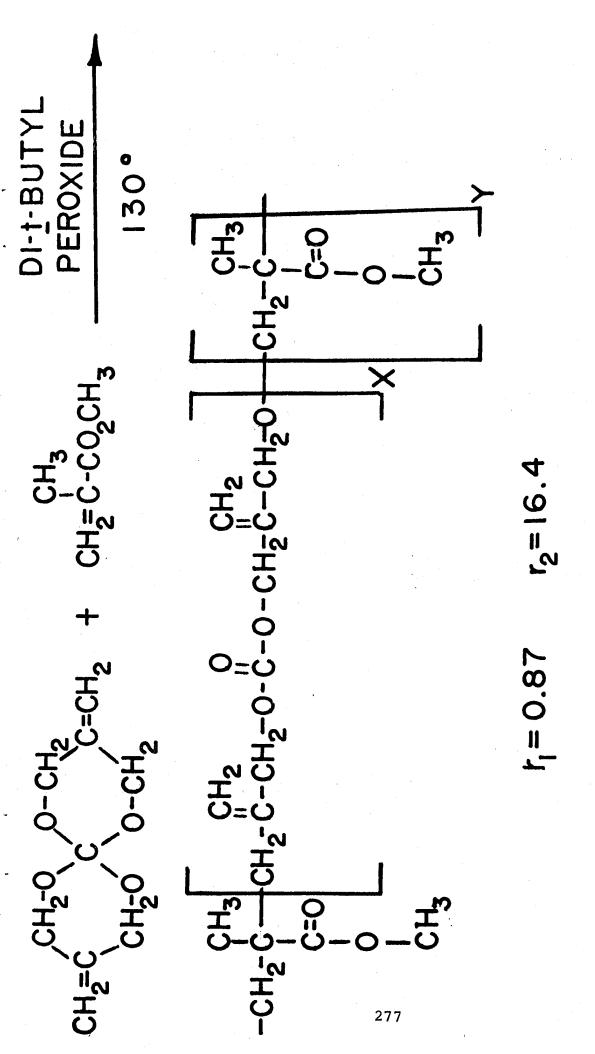


$$\begin{bmatrix} CH_2 & CH_2 & CH_2 \\ -CH_2 & CH_2 \\ -CH_2 & CH_2 \end{bmatrix} \times \begin{bmatrix} CH_2 & CH_2 \\ -CH_2 & CH_2 \\ -CH_2 & CH_2 \end{bmatrix}$$

$$CH_2 = C$$
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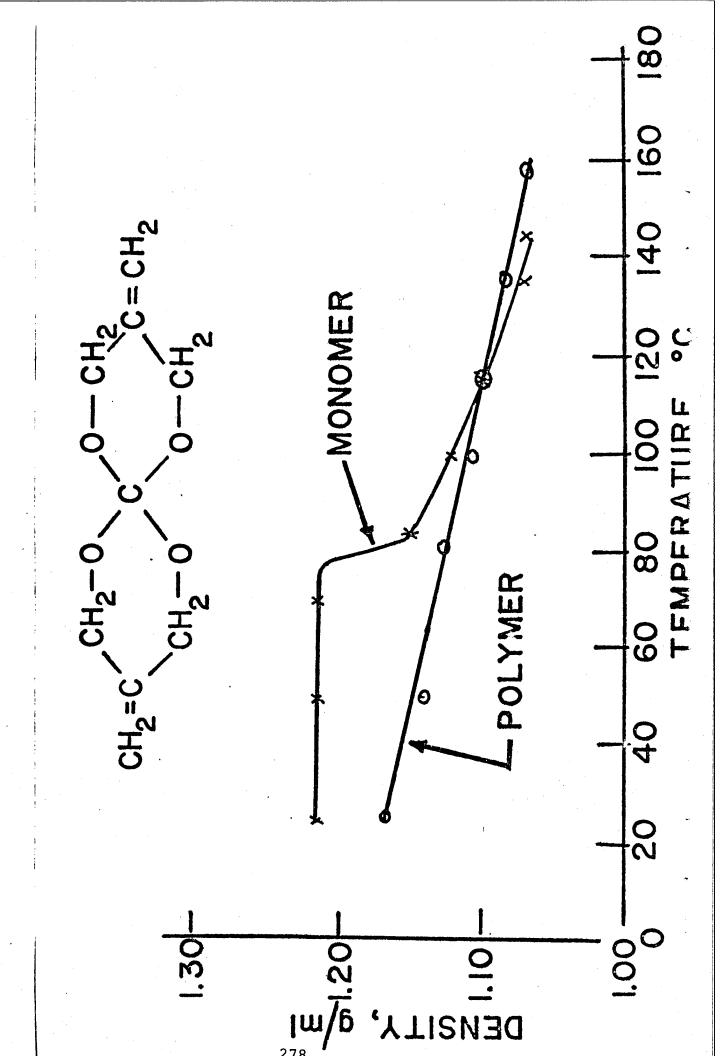
80% SOLUBLE; | η | =0.24 (CHCI3,25°





FEED GIVES 1% CARBONATE IN COPOLYMER 69% CONVERSION, 10% SPIRO MONOMER IN

AND RELATED POLYOXYCARBONATE VERSUS TEMPERATURE THE MONOMERIC SPIRO ORTHO CARBONATE DENSITIES OF



MATERIALS DEVELOPMENT REQUIREMENTS AIRBORNE CARBON/GRAPHITE FIBERS

M. T. KATSUMOTO

BOEING COMMERCIAL AIRPLANE CO.

MARCH 23, 1978

Mul Katsumoto Boing Commercial Amplanc G.

MATERIAL DEVELOPMENT REQUIREMENTS AIRBORNE CARBON/GRAPHITE FIBERS

o PHASE I NEAR TERM REQUIREMENTS

CONTINUE WITH EXISTING EPOXY AND FIBER SYSTEM

- ESTABLISH VIABILITY OF HYBRIDIZATION, VARYING WEAVE AND TAPE FORMS, APPLICATION OF SUPPLEMENTAL COATING, ETC.
- DHASE II LONG TERM REQUIREMENTS
- MODIFICATION OF CURRENT EPOXY AND FIBER SYSTEMS
- DEVELOP NEW MATRIX AND FIBER SYSTEMS

RATIONALE - PHASE I

CONTINUE WITH EXISTING EPOXY AND FIBER SYSTEMS:

- DISPERSAL AND FRAGMENTATION PHENOMENA NOT COMPLETELY UNDERSTOOD
- DIFFERENT WEAVE AND TAPE COMBINATION FORMS
 - HYBRID TAPE AND FABRIC
- SUPPLEMENTAL COATING SYSTEM
- HARDWARE COMMITMENT ON CURRENT AND PROPOSED AIRPLANES 0
- COMPOSITE TECHNOLOGY JEOPARDIZED IF CONTINUITY IN COMMITMENT NOT MAINTAINED
- LONG LEAD TIME REQUIRED-MATERIAL DEVELOPMENT TO CERTIFICATION
- **EVALUATION**
- SPECIFICATION
- DESIGN

MINIMUM OF 5-7 YEARS

- DURABILITY
- ALLOWABLES
- CERTIFICATION
- EXTENSIVE DATA BASE REQUIRED FOR AIRPLANE CERTIFICATION

TECHNICAL REQUIREMENTS

- IF REQUIRED IMPROVE AFTER BURN PROPERTIES TO CONTROL FRAGMENTATION AND DISPERSAL OF FIBERS 0
- O INHERENT RESISTANCE TO AIRCRAFT FLUIDS

HYDRAULIC FLUIDS

ANTI-ICING

COMPATIBLE WITH AIRCRAFT ENVIRONMENTS

MOISTURE TEMP. (-65° to 180°F)

COMPATIBILITY WITH AIRCRAFT MATERIALS

PAINT

SEALANT

ADHES IVES

ALUMINUM

TITANIUM

COMPOSITE

EXHIBIT COST EFFECTIVE MANUFACTURING PROCESS

MATERIALS COMPATIBILITY

PHOSPHATE ESTER HYDRAULIC FLUIDS

PROPERTIES

LOW VOLATILITY

LOW SURFACE TENSION

EXCELLENT SOLVENT

MISCIBLE WITH OTHER SYNTHETIC COMPOUNDS

PLASTICIZER (PARTICULARLY FOR POLYVINYL TYPE RESINS)

FIRE RESISTANT

diButyl C4H9-0 \
Phenyl C4H9-0 - P = 0
Phosphate <-> -0 <->

tri Butyl C4H9-0 Phosphate C4H9-0 - P = 0 C4H9-0 tri Cresyl CH₃ \bigcirc -0Phosphate CH₃ \bigcirc -0 -P=0

FLUID COMPATIBILITY

PERCENT SWELL - 72 HOURS AT 160°F

	PHOS PHATE ESTER HYDRAULIC FLUIDS (SKYDROL 500 TYPE)	TYPE III FUEL
NEOPRENE	150%	81%
HYPALON	250%	100%
ВИТУL	7%	403%
VITON	225%	3%
POLYIMIDE	- 0.04%	
ETHY LENE PROPY LENE	4.5%	315%
EPOXY 350 ⁰ F	. 55%	
ARC 160	1.1%	
* POLY SULFONE * TITANIUM	- 2.07% 0%	

** Embrittlement problems at high temperatures

* Unsatisfactory under stress conditions

RATIONAL PHASE II

- & MECHANICAL PROPERTIES TO EXPAND USAGE TO PRIMARY STRUCTURE O IMPROVE ENVIRONMENTAL DURABILITY, FRACTURE TOUGHNESS
- IMPROVE FLAMMABILITY RESISTANCE FOR INTERIOR AND FLAME CRITICAL AREAS (FUEL TANK, POWER PLANT, APU, ETC.) 0
- O IMPROVE LIGHTNING STRIKE AND ELECTRICAL EFFECTS
- IF REQUIRED IMPROVE AFTER BURN PROPERTIES TO CONTROL FRAGMENTATION & DISPERSAL OF FIBERS 0

PRELIMINARY TECHNICAL		REQUIREMENTS - PHASE	HASE	.			
	CUR	CURRENT EPOXY SYSTEM	>-	PROP	PROPOSED C	SE II COMPOSI TEM	TE
COMPOSITE PROPERTIES	TAPE	FABRIC	IC	AT.	TAPE	FABRIC	2
TENSILE ULT 0° RT	185	. 70	0	2	200	0.6	
TENSILE MODULUS 0° RT	18 - 21	8.5	F	18	- 21	9-11	
TENSILE STRAIN 0° RT	9500	7000	0	100	0000	8000	
TENSILE 90° R.T.	4.5 KSI	70	0		5	90	
SHORT/BEAM/SHEAR	۲ ۲		7		14	ω	
COMPRESSION 0°	155	70	0		170	80	
COMPRESSION (MODULUS)	16.5-19	7.5-1	0 [19	- 22	16.5-1	9
COMPRESSION STRAIN	8500	. 6800	0	10,	000	8000	
MOISTURE RESISTANCE	+45 SB	S COMP.	SBS	+45	SBS	COMP	SBS
				Tens.			
& REIENTION OF STRENGTH @ RT	85 75	80	80	9.2	9 2	95	9 5
KE LEIN I I O'N	2	-	50	85	85	85	
LIGHTNING STRIKE-ELECTRICAL EFFECTS	ON	N.	0	>	es	γe	Л
FLUID RESISTANCE		- No					
FUEL	Yes	نه ا	5	>	Yes		
SKYDROL	Yes	γe	S	>	es	Ye	\(\sigma\)
FIBER FRAGMENTATION & DISPERSAL	80N	10V	~:	Y	es	۲e	S
FLAMMABILITY FAR 25	80N	NO?	~	>	Yes	Ye	S

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	9					ITY TE			•	<	FAA PREPRODUCTION CERTIFICATION	FL 1GHT	
SCHEDULE			•			DURABIL	UPDATED ALLOWABLES		PRODUCTION COMMITMENT	NO			
	ഹ	•	.*			1.1	UPDA ALLO	N D I	PROD	PREPRODUCTION			
PMENT			•		TION	ENVIRONMENTAL		T DESIGN	_	PREPR(
DEVELOPMENT	4		15 17 I O N	•	ECIFICATION RELEASE	1 1.	PRELIMINARY ALLOWABLES	PROJECT		,			
ATERIAL		•	CT SYSTEMS QUALIFICAT	PREP.	SP	LLOWABLES,	PRELI ALLO	i i					
MAT	က	•	SELECT FOR OUP	VARY PR	IFICATION JPPLIERS	ALLO		•			¥		_,
	1		ES S	PREL IMINARY SPECIFICA	QUALIFICA OF SUPPLI				• .				•
	2		DAT	d	•				•			•	
		•	EVALUZ CANDI						•				
		QMTS EFINED			•	-		•			,		•

HYBRID COMPOSITES Dr. KARL PREWO, CHAIRMAN

NAME

ORGANIZATION

Karl Prewo United Technologies Research Ctr.

William E. Winters TRW Equipment

John Wooley Lockheed Calif. Co.

Harold Sanders Grumman Aerospace

Karl Hergenrother Transportation Systems Center - DOT

John Freche NASA Lewis Research Ctr.

Jim McGann Rockwell International (LAD)

Charlie King NASA LaRC

Jim Henshaw AVCO Specialty Materials Div.

Ashok Dhingra DuPont

Ira Petker Composites Horizons

NASA Reporters: A. J. Chapman and W. B. Lisagor, LaRC

ISSUES FOR

HYBRID COMPOSITES

WORKING GROUP

- 1. What principles would be employed by hybrid composites to retard fiber release?
- 2. Would metallic coatings applied to the surface of fabricated parts be effective in retarding fiber release?
- 3. Would intumescent coatings applied to the surface of fabricated parts be effective in retarding fiber release?
- 4. For each potential solution via hybridization:
 - (a) What principle would this approach employ to retard fiber release?
 - (b) What is the likely effect on the weight of fabricated parts?
 - (c) Would this approach be cost effective?
 - (d) How difficult would it be to fabricate this hybrid?
 - (e) What effect would this approach have on mechanical properties?
 - (f) What is the likely environmental durability of this hybrid as compared to graphite-epoxy?
 - (g) Are any large scale production problems likley with this hybrid?
- 6. What is your assessment of the current NASA research program in this area, and what changes do you recommend?
- 7. Rank the generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS' SUMMARY FOR HYBRID COMPOSITES WORKING GROUP

Prior to the general working group discussions, Ashok Dhingra presented a prepared review of DuPont's Kevlar and FP (Al₂O₃) fiber development (see Coatings Section for copy of visual aids). These fibers are being advanced as possible replacements for graphite or for use in hybrid laminates.

The working group focused mainly on ways to contain the graphite fibers and prevent their dispersion to the environment following damage, fire or explosion. The particular hybrid systems discussed included metallic surface layers, third material additives, intumescent coatings, outer composite envelope, multiple fiber hybrids, and resin hybridization.

Metallic Surface Layers. Metal foils or wire mesh may be applied to composite surfaces to prevent graphite fiber dispersion by maintaining surface integrity. Such surfaces are presently incorporated in some composites for lightning damage protection, and they do not involve critical modifications to the basic composite. Disadvantages include the possiblity that the metal surfaces would not be effective in case of extreme damage, and may cause distortion during laminate fabrication.

Third Material Additive. Structurally passive particulate or fiberous additives may prevent dispersion of graphite fibers in case of fire by melting and fusing over the fibers. Such additives include a glass fiber screen or weave, glass microballoons or solid particles, and a fiber "serving" or coating. This approach would require minimum changes in the matrix and in processing, and may require only minimum requalification of the composite. However, laminate density would be increased and specific properties would be decreased. The additives may contribute to fiber damage in normal service.

Intumescent Coatings.— An organic coating (~ .03") may be applied to the composite surface to minimize dispersion of graphite fibers in the event of damage and fire. Such coatings may be an immediate quick-fix for existing composite components and, although not a complete solution, these coatings may enable the continuation of existing composite flight programs. Apparent disadvantages of intumescent coatings include additional weight and short service life. It was also agreed that it would be difficult to keep the coating on.

Outer Composite Envelope. Structurally active outer composite plies may be used to contain inner graphite fiber plies in the event of fire and damage. The outer plies would consist of fire resistant fibers in a high char forming resin matrix. This approach has the advantage of adding a structurally active part to the composite rather than passive weight. Possible disadvantages may include compatibility with graphite plies, weight, and cost.

Multiple Fiber Hybrids. - Non-conducting fibers may be used in combination with graphite to reduce the amount of conducting fibers released by a fire to some acceptable level. This approach would have the advantage of retaining many of the superior properties of graphite fibers, while possibly gaining some unique properties from a new fiber. For example, high modulus - low strength fibers would be combined with low modulus - high strength fibers. Laminates could be designed for ply combinations using various fibers.

Resin Hybridization.— This approach would involve distributing layers of different resin systems throughout the laminate. Most of the discussion centered on high char yield resins. Discrete layers of high char forming resin would be distributed between conventional plies throughout the laminate. In the event of fire, the resulting char may adhere to graphite fibers retarding their disperion. After some consideration, this approach did not seem too attractive; inclusion of such layers would probably lower fiber content, degrade mechanical properties, and require a new data base. Using a high char forming resin matrix throughout the composite appeared to be a better approach but would not be classified as a hybrid composite.

CONCLUSIONS

- 1. Hybridization is the only reasonable approach for a near term solution to the graphite fiber problem.
- 2. Significant changes in the graphite/epoxy system would destroy the utility of the data base and would require new material qualification programs.
- 3. Replacement of graphite fibers would result in inferior mechanical properties and replacement of the epoxy would reduce the efficiency of the composite. The advantages of composites would be destroyed.

- 4. Metallic coatings for containing fibers are probably not satisfactory.
- 5. Glass cloth or fiber outer layers may offer the most promise for preventing release of graphite fibers.

RECOMMENDATIONS

- 1. Promising solutions should be implemented in the short term to maintain impetus of existing programs avoiding dissumptions which could jeopardize program support.
- 2. Standardized tests must be developed to define the graphite fiber hazard potential as well as to evaluate potential fixes.
- 3. The hazard potential must be evaluated with respect to various aircraft zones (structure, systems, engines, etc.).
- 4. Continue research on long term optimum solutions while implementing short term solutions.
- 5. Long term solutions should consider epoxy resin replacement, alternate or modified fibers, new hybrids.

REPORT OF

HYBRID COMPOSITES WORKING GROUP

DR. KARL PREWO, CHAIRMAN

HYBRID COMPOSITES

ISSUES CONSIDERED

FIND SOLUTION THAT CAUSES MINIMUM DISRUPTION OF

EXISTING TECHNOLOGY BASE

LONGER TERM SOLUTION

0

INTUMESCENT COATING

APPROACH

USE AN ORGANIC COATING THAT MINIMIZES THE LIKELIHOOD OF BURNING AND ALSO THE ESCAPE OF GRAPHITE FIBERS.

ADVANTAGES

O VERY QUICK FIX

CAN BE APPLIED TO EXISTING COMPONENTS

DISADVANTAGES

WEIGHT PENALTY

0

SHORT SERVICE LIFE

0

0

METALLIC SURFACE LAYERS

APPROACH

PREVENT FIBER ESCAPE BY MAINTAINING SURFACE INTEGRITY

- O METAL FOIL OR WIRE MESH
- O METALLIZED GLASS FIBERS

ADVANTAGES

- O MAY ALREADY BE DESIGNED IN
- MEETS LIGHTNING PROTECTION REQUIREMENTS
- NO COMPOSITE MODIFICATION

0

IMPROVED IMPACT TOLERANCE

UISADVANTAGES

- EXTREME DAMAGE MAY OVERCOME
- MAY CAUSE DISTORTION

THIRD MATERIAL ADDITIVE

APPROACH

PREVENT ESCAPE OF GRAPHITE THROUGH USE OF PARTICULATE OR FIBROUS ADDITIVE WHICH IS PASSIVE EXCEPT IN THE CASE OF FIRE

GLASS FIBERS - SCRIM - "UNIWEAVE"

0

- O FIBER "SERVING"
- MICROBALLOONS OR SOLID PARTICULATE

0

ADVANTAGES

- O MINIMUM REQUALIFICATION
- O MINIMUM CHANGE IN MATRIX AND PROCESSING
- NO CHANGE IN FIBER

DISADVANTAGES

- O INCREASED WEIGHT
- O FIBER DAMAGE

OUTER COMPOSITE ENVELOPE

APPROACH

USE "ACTIVE" OUTER COMPOSITE LAYERS AS CONTAINMENT.

O HIGH CHAR FORMING RESIN MATRIX PLIES

O FIRE RESISTANT FIBERS IN OUTER PLIES

(E.G. B, GLASS)

ADVANTAGES

O CONTRIBUTES STRUCTURALLY

DISADVANTAGES

O COST PENALTY

O WEIGHT PENALTY

MULTIPLE FIBER HYBRIDS

APPROACH

USE NON CONDUCTING FIBERS IN COMBINATION WITH OR WITHOUT GRAPHITE FIBERS

<u>ADVANTAGES</u>

SOME FIBERS CURRENTLY AVAILABLE

UNIQUE PAY OFFS (TOUGHNESS)

DISADVANTAGES

REQUIRES REDESIGN

INCOMPLETE KNOWLEDGE OF FAILURE MECHANISMS

INFERIOR SPECIFIC PROPERTIES MAY NOT BE ACCEPTABLE

0 0

RANKING OF GENERIC SOLUTIONS

SOLUTION	% PARTICIPANTS <u>FAVORING</u>
HYBRIDS	04
EPOXY MODIFICATION	. 15
"EXISTING" REPLACEMENT RESINS	15
FIBER MODIFICATIONS	10
FIBER COATINGS	10
ALTERNATE FIBERS	10

RECOMMENDATIONS

S IN THE SHORT TERM TO MAINTAIN	14.
SHOR	•
北	
Z	
FIND PROMISING SOLUTIONS	COMPOSITE IMPETUS
0	

O HYBRIDS OFFER BEST OPPORTUNITY TO ACHIEVE THIS

WEED REPRESENTATIVE TESTS THAT CAN BE STANDARDIZED 0

O ZONE HAZARD LEVELS OF AIRCRAFT AND ENGINES

LOOK FOR LONG TERM SOLUTION - ALTHOUGH SHORT TERM MAY SUFFICE 0

MAINTAIN VISIBILITY

0

FIBER RELEASE SIMULATION TESTING E. Bruce Belason, Chairman

NAME

Bob Schaffer

ORGANIZATION

Raymond Foye U.S. Army R&T LABS T. C. Grimm McDonnell Aircraft Co. Robert E. Sanders Rockwell International - Tulsa Frank Riel Rohr Industries, Inc. H. C. Schjelderup Douglas Aircraft Co. Richard Tracy Lear Avia Corp. William J. Snyder Bucknell University Joe Mansfield NASA Ames Vernon Bell NASA Larc Bill Brooks NASA Larc Tito Serafini NASA Lewis Bruce Belason AVCO Specialty Materials Div. Wolf Elber NASA Larc Joseph Reardon Naval Res. Lab Ken Musselman Naval Surface Weapons Ctr (Dahlgren) Edward Lopez Lockheed Calif. John McFerrin Union Carbide John Parker NASA Ames James Peterson Boeing Commercial Airplane Co. Guilio Varsi JPL Dell Williams NASA Headquarters

HITCO Defense Products

NASA Reporters: Robert Jewell and Don Rummler, LaRC

ISSUES FOR

FIBER RELEASE SIMULATION TESTING

WORKING GROUP

- 1. Can fiber release testing be realistically simulated?
- 2. What procedure do you recommend for laboratory scale testing? Are there alternative procedures? What are the advantages and disadvantages of each?
 - (a) How should we conduct laboratory tests to reproduce the effects of fire and explosion on coated or treated fibers?
 - (b) How should we screen the fiber release characteristics of hybrids or new resins in the laboratory?
- 3. What quick, relatively inexpensive, large scale tests can be used to screen resin modifications and hybrids for effectiveness in reducing fiber release?
- 4. What procedure do you recommend for large or full scale qualification testing? Are there alternative procedures? What are advantages and disadvantages of each?
- 5. What test temperatures, oxidation rates, burning times, smoke generation rates, flame oxygen content, and fiber dissemination procedures should be used in a simulation facility?
- 6. What are reasonable and appropriate specimen sizes, shapes, resin contents for each scale of testing?
- 7. What inputs are needed from risk analysis to evaluate the effectiveness of materials modifications?

NASA REPORTERS' SUMMARY FOR FIBER RELEASE SIMULATION TESTING WORKING GROUP

The meeting was prefaced with 5 presentations given by Jim Peterson (Boeing), Bruce Belason (AVCO), Joe Reardon (NRL), Guilio Varsi (JPL) and Joe Mansfield (NASA-Ames). The working group's deliberations are summarized in three parts according to the particular test parameter: burn conditions, fiber release mechanisms, and measurements on released fibers.

Burn conditions.— A concensus was reached on (a) the urgent need to establish a set of laboratory test procedures, and (b) the urgent need for risk analysis studies. The risks associated with release of graphite fibers in an aircraft accident are ill-defined. Bounds establishing the nature of a reasonable threat are needed as initial guidelines for selecting testing parameters.

For the composite materials in present use, the effects of variations in test temperature, flame oxygen content, heat flux, and other parameters should be determined and documented. It was agreed that NASA should take the lead in developing simulated test methods. Detailed issues, such as appropriate specimen geometry, types of large-scale tests, and methods for testing specific materials, e.g., hybrid laminates or composites composed of coated or treated fiber, were not discussed.

Fiber release mechanisms.— In the combustion of the composite material, the matrix resin is burned, with no fiber release occurring. Fiber dispersal requires some form of agitation during or after combustion.

Fiber release by detonation of an explosive charge is a violent method, tending to distort test results. Dissemination of fibers by mechanical vibration, by air currents or air blasts, by falling or swinging weights, and by other projectiles are some alternative methods. The working group did not select a preference.

Laboratory test methods are needed to simulate the effects of a large scale fire phenomena. Then, test methods to adequately simulate fiber release could be developed. A description of the thermal/physical environment (scenarios) considered most relevant to the problem is critically needed in order to select test parameters.

Measurements on released fibers. - Laboratory simulation of the burn and fiber release is not the main problem.

Methods and/or instruments for collection of meaningful data on fiber release represent a true bottleneck. Those now testing yearn for a "fiber dosimeter." Measurements of fiber release phenomena at present are rudimentary and crudely qualitative. Meaningful testing must discern fiber geometries and their distribution, fiber quantities, and fiber electrical properties. Applicable test methods and instrumentation are needed.

CONCLUSIONS

- 1. A set of laboratory test procedures is urgently needed. However, selection of suitable test conditions requires inputs from risk analysis as well as parametric data for various burning and impact conditions.
- 2. Further definition of the risk resulting from the carbon fiber hazard is necessary before companies will take strong independent roles in testing. In the meantime, NASA must play a major role in guiding and financing development in this area.

RECOMMENDATIONS

- 1. A working group of reasonable and effective size should be established to develop test methods and procedures. NASA should be charged with this duty.
- 2. The participants strongly suggested that the aircraft industry will not address problems associated with the accidental release of graphite fiber unless the problem area is more competently defined. The participants indicated that definition of the threat should be an NASA activity.

REPORT OF

FIBER RELEASE SIMULATION TESTING WORKING GROUP

E. BRUCE BELASON, CHAIRMAN

FIBER RELEASE SIMULATION TESTING

GENERAL SCOPE OF ISSUES

1,) CAN FIBER RELEASE TESTING BE DONE SUCCESSFULLY?

i) SMALL SCALE/LAB/SCREENING TEST

SUPPORT RISK ANALYSIS ii) LARGER SCALE/FIELD/HARDWARE TEST ETC. EDGE EFFECTS ORIENTATION SHAPE TEST SPECIMEN DESIGN: SIZE 2.)

3.) TEST CONDITIONS:

TEMP, (OF FIRE)

HEAT FLUXES: CONVECTIVE

THERMAL:

TIME

CHEMICAL: OXIDATION EFFECTS

BEFORE

MECHANICAL PERTUBATIONS: DURIN

DURING BURNING?

AFTER

4.) WECESSARY DEGREE OF AWALYSIS OF FIBER RELEASE?: CATCH ALL FIBERS ANALYZE

PRE/POST TEST SPECIMEN ANALYSIS

FIBER RELEASE SIMULATION TESTING (Continued)

5.) TEST FACILITIES AND TECHNIQUES FOR THE ABOVE:

			IF DEV'T I	IF DEV'T IS REQUIRED:
STATUS	SMALL SCALE	LARGE SCALE	LSOO	TIME
EXISTING				
EXISTING, BUT REQUIRE MOD,	×	\cdot\;		3 MOS.
MUST BE BUILT (OR DEVELOPED)	ſ	\ \ 		

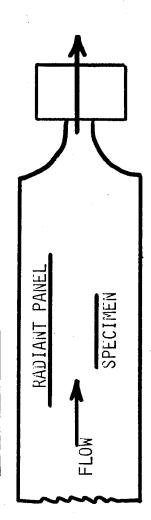
6.) RISK ANALYSIS INTERFACE: INPUTS REQUIRED

OUTPUTS REQUIRED

MATERIALS SCREENING TEST (CONSENSUS)

FACILITY DESIGN

FIBER COLLECTION



TEST CONCLUSIONS TO DATE:

LEAVING FIBERS WHICH APPEAR TO BE READILY REMOVABLE IF MECHANICALLY IN CURRENT GRAPHITE/EPOXY, RESIN BURNS OUT QUICKLY (3 MINUTES), PERTURBED.

EXPERIMENTAL NEEDS:

- IMPROVED DIAGNOSTICS FOR FIBER RELEASE MEASUREMENT,
- CORRELATION OF MEASURED FIBER RELEASE TO REAL LIFE ENV'TS,

UNRESULVED:

WHETHER TO INCORPORATE MECHANICAL PERTURBATION AND IF SO, WHAT TYPE?

ACTION RECOMMENDED:

HASA TO FORM A WORKING GROUP

RISK ANALYSIS TEST

TEST FACILITY DESIGN

LARGER SPECIMENS (VS SCREENING TEST)

0

- VARIOUS SHAPES
- VARIOUS MECHANICAL IMPACTS (SIMULTANEOUS TO FIRE EXPOSURE)
- INCORPORATE FIBER RELEASE DIAGNOSTICS
- RESULTS MUST BE EXTRAPOLATABLE TO RELIABLY ANALYZE POTENTIAL ACCIDENT SCENARIOS.

OTHER FACTORS/CONSIDERATIONS

0

- RISK ANALYSIS MUST CONSIDER WHAT PARTS OF AIRPLANES ARE TO COMPOSITES AND IN WHAT FORM, AND WHAT TYPE OF SCENARIO(S) THIS COMPONENT CAN LIKELY SEE, FIRE
- FIBER TRANSPORT (AFTER RELEASE) MUST BE DETERMINED
- CRITICAL FIBER SIZES MUST BE BETTER DEFINED
- CREDIBILITY GAP EXISTS

FIRE AND IMPACT TESTING

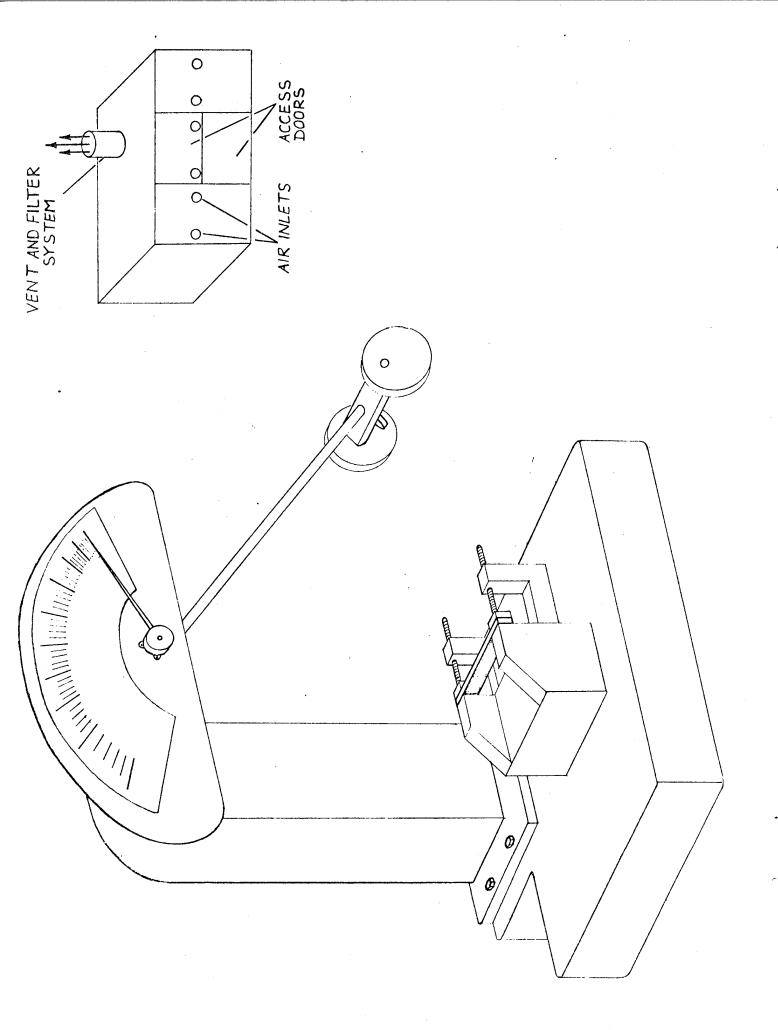
JOE MANSFIELD (ARC)

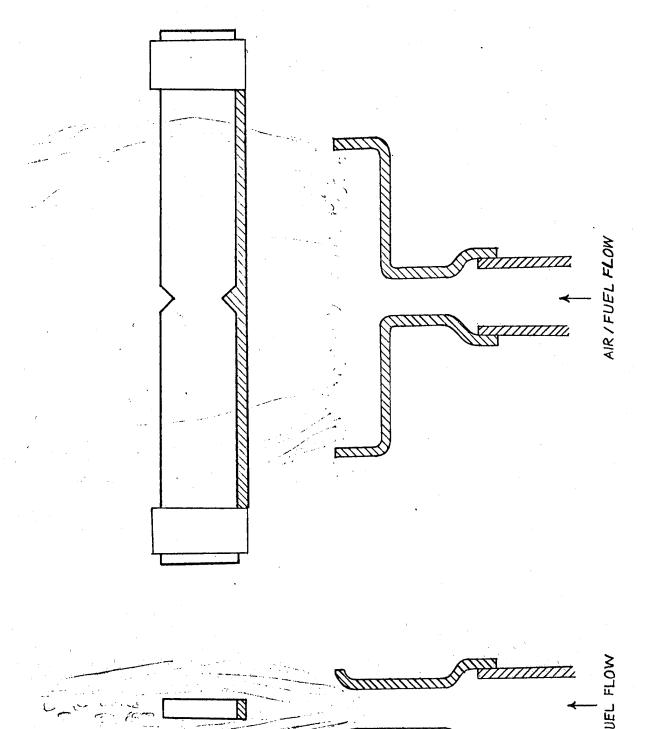
MARCH 23, 1978

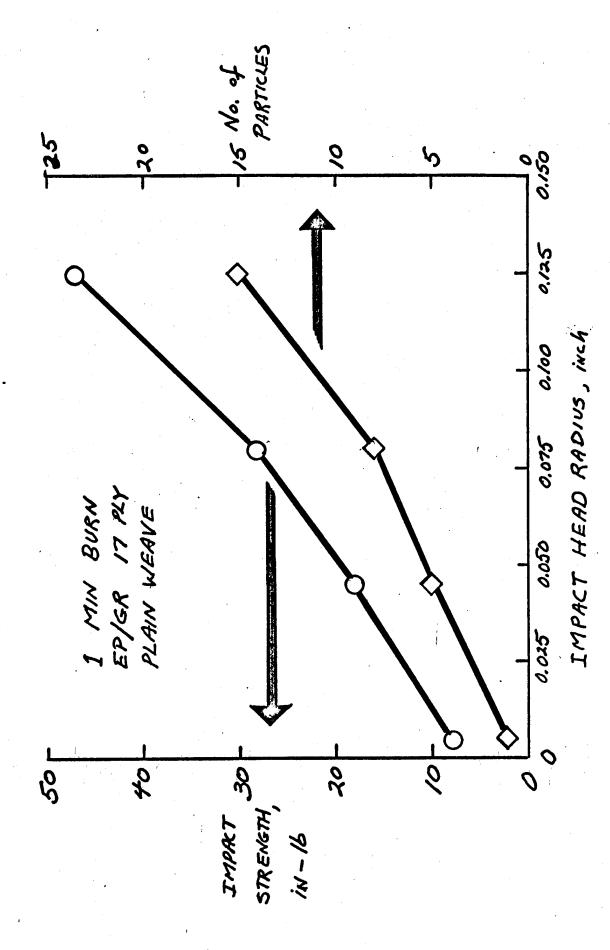
SCREENING		SIMULA FION
	CONSIDERED &	
	£375	

REALISM OF FIRE EXPOSURE	REALISM OF MECHANICAL EXPOSURE	REALISM OF SAMPLE CONFIGURATION AND SUPPORT MECHANISMS	TEST TIME REQUIRENENTS	COSTS OF MANUFACTURE AND OPERATION
		TEST PARAMETERS		

MODIFIED CHARPY INPACT (BURNING SAMRES) STANDARD MECHANICAL TESTS (UNBURNED SAMPLES) 50-400 FT/Sec CHARPY IMPACT (UN MODIFIED) ~ 30 FT/Sec HIGH VELOCITY FLOW EXPOSURE TESTS XYONX LABORATORY FLAMMABILITY EXPOSURE LIMITIME OXYGEN PROJECTILE IMPACT TENSILE FLEXURG SHOCK WAVE SMALL-SCALE SCREENING SIMULATION! Tests TESTS







RECOMMENDED SPECIFICATIONS FOR TEST IMPACT ノルカグライン

1,4,5	205. √	/25	200 m-16	PROPANE	•	
THICKNESS	WIDTH AT NOTCH	IMPACT HEAD RADIUS	IMPACT ARM WEIGHT		FLOW RATE	FLOW RATE
SAMPLE	SAMPLE	IMPALT	IMPACT	FUEL	FUEL	AIR FL

resr CHARPY SCREENING MODIFIED

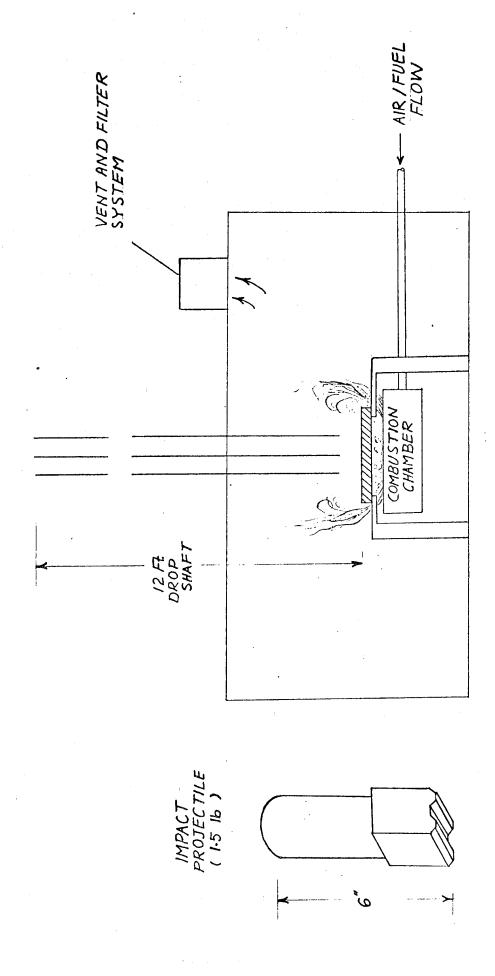
COMMERCIAL INSTRUMENT WITH MINDE MODIFICATION BOTH DURING AND AFTER BURNING resr SE ADVANTAGES

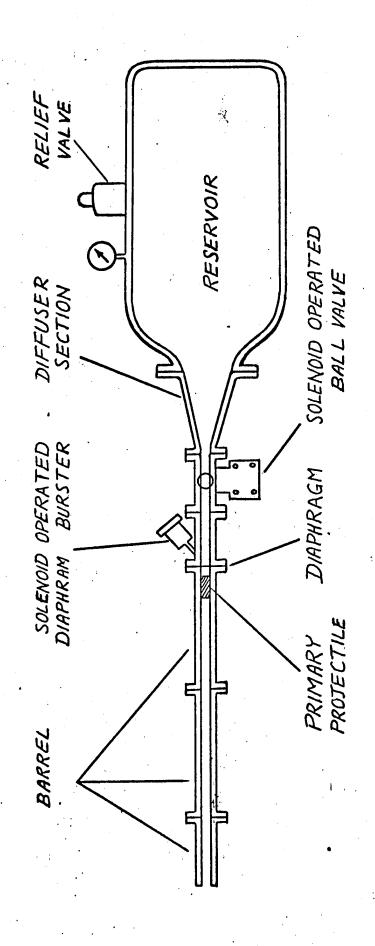
SMALL AND EASILY FABRICATED SAMPLE ISE

TESTING TIME 5m364 REA SONABLY

NOT COVER FULL RANGE OF MECHANICAL EXPOSURES FIRE EXPOSURE REPLICATION FULLY SIMULATE FAIRLY EXTENSIVE 6 DIFFICULT REGUIFES DOES

DISADVANTAKES





BURNER CONFIGURATION FOR SIMULATION

FIBER RELEASE SIMULATION TESTING

JAMES M. PETERSEN
BOEING COMMERCIAL AIRPLANE CO.

MARCH 23, 1978

ABSTRACT Fiber Release Simulation Testing James M. Peterson, Boeing

The level of risk involving current technology graphite/epoxy hardware on commercial aircraft, due to the "floating fiber" phenomenon, has not been established. Resolving this question must be done by a systematic study that addresses the probability that the hardware is involved in a fire resulting in the release of fibers, that the fire is near a site housing vulnerable electrical components, and that loss or damage occurs due to any resulting electrical failure.

The type of thermal/physical environment that can result in substantial fiber release must be understood before a risk assessment can be made. Available files containing accident data should be utilized to determine the historical frequency of accidents in which composite hardware, had it been present, might have been involved. The pre-, during, and post-fire parameters that affect fiber release must be defined and evaluated. Appropriate laboratory test methodology is needed for research and development that can simulate the effects of large scale fire phenomena on fiber release, and on the subsequent transport of the fibers away from the fire site.

GRAPHITE/EPOXY HARDWARE ON COMMERCIAL AIRPLANES

LEVEL OF RISK HAS NOT BEEN ESTABLISHED

PARAMETERS (PROBABILITIES) AFFECTING RISK

- AIRCRAFT ACCIDENT OCCURENCE
- O FIRE INVOLVED
- O GRAPHITE COMPOSITE INVOLVED IN FIRE
- O FIRE/PHYSICAL ENVIRONMENT CAUSES FIBER RELEASE
- O RELEASED FIBERS TRANSPORTED FROM FIRE SITE
- O VULNERABLE ELECTRICAL COMPONENTS IN TRANSPORTED FIBER PATH
- ELECTRICAL FAULTING OR FAILURE OCCURS
- O LOSS RESULTS FROM FAULT OR FAILURE

DEVELOPMENT OF OCCURRENCE DATA AND REPRESENTATIVE AIRCRAFT ACCIDENTIFIRE DAMAGE SCENARIOS

Establish the probability of aircraft accidents involving fires, composite structure and composite part damage based on accident data and composite materials useage forecasts.

Develop scenarios based on accident histories to provide representative fire, intensity and duration, structural involvement, structural damage, additional damage aspects such as explosion or fire fighting.

REQUIRED OUTPUT:

- 1. Probability of occurrence of representative conditions
- Series of representative scenarios
 - 3. Representative test conditions

DATA SOURCES:

- Accident statistics files (NTSB & Others)
 Accident reports
- 3. Accident investigator statements
- Photo records of accidents

ESTABLISHMENT OF TEST MITHODOLOGY REQUIRES

- DEVELOPMENT OF OCCURRENCEDATA AND REPRESENTATIVE AIRCRAFT ACCIDENT/FIRE DAMAGE SCENTRIOS
- DETERMINATION OF CONDITIOIS IN FIRE ENVIRONMENT IN SCENARIO!
- ESTABLISHMENT OF SMALL SCALE TESTS THAT REPRODUCE CONDITIONS IN LARGE SCALE FIRES

DETERMINATION OF CONDITIONS OF FIRE ENVIRONMENT IN SCENARIOS

duration, ventilation, etc. To determine parameters needed for design Establish the fire environment in scenarios based on fire intensity,

representative tests.

REQUIRED OUTPUT:

Representative test conditions

DATA SOURCES:

I. Accident statistics files (NTSB & Others)

. Accident reports

3. Data from Large-Scale experimental fire test

ESTABLISHMENT OF SMALL SCALE TEST METHODOLOGY TO SIMULATE --- CONDITIONS IN LARGE SCALE FIRES

OBJECTIVE: Estab

Establish small scale test apparatus, conditions, and procedures that can be utilized to assess the effects of large scale fires on

composite materials.

REQUIRED OUTPUT:

1. Test apparatus and methodology

DATA SOURCES:

1. Current fire R&D pertaining to aircraft

2. Standard reference works

- AMOUNT OF FIBER RELEASED
- RELEASED FIBER PHYSICAL CHARACTERISTICS
- o SINGLE, MULTI PLE o LENGTH.
- RELEASED FIBER ELECTRICAL CHARACTERISTICS

DEVELOP ENTRAINMENT, REENTRAINMENT, TRANSPORT DATA AND RELATE TO POTENTIAL PROBLEM SITES

- 1. Using the characteristic fiber release develop entrainment models and assumptions-generate entrainment data.
- 2. Using the characteristic fiber release develop reentrainment models and assumptions-generate reentrainment data.
- 3. Identify and select representative transport models with appropriate assumptions.....
- 4. Identify representative potential problem sites.

REQUIRED OUTPUT:

- 1. Tabulation of entrainment, reentrainment data for characteristic fibers.
- 2. Selected transport model with assumptions.
- Characteristic potential problem sites-accident aircraft, other aircraft, air control equipment, community locations.

DATA SOURCES:

- 1. Standard entrainment, reentrainment models
- . Standard transport models
- 3. Standard reference works

FIRE TESTING OF GRAPHITE-EPOXY COMPOSITES IN AVCO'S MODEL 25 FIRE TEST FACILITY

Ву

E. Bruce Belason

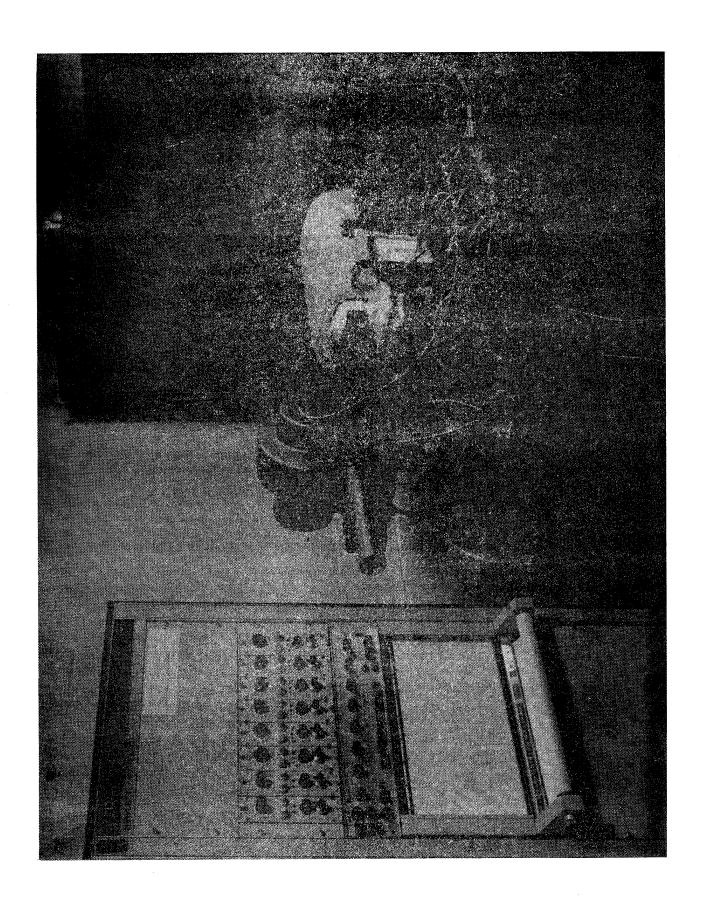
Avco Specialty Materials Div.

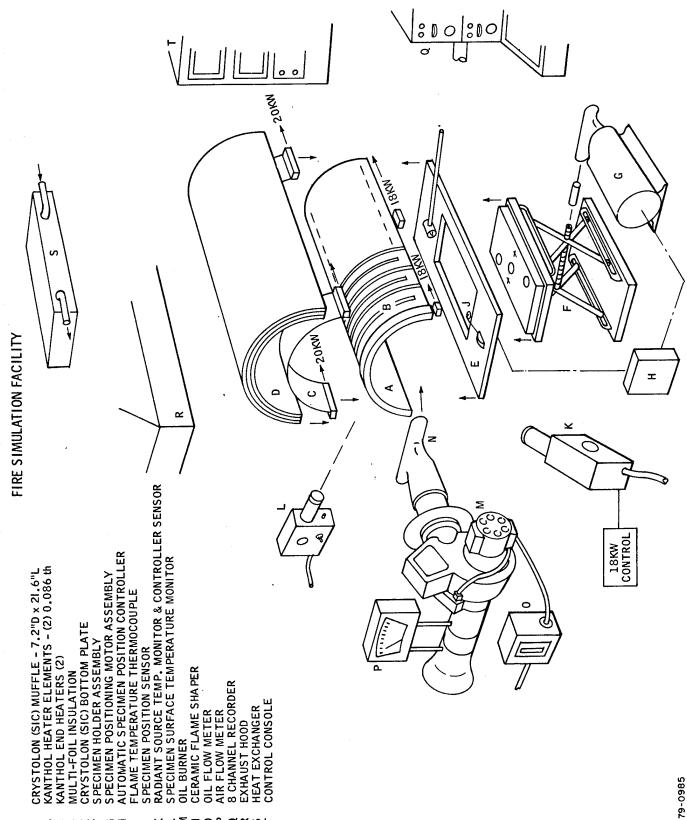
March 23, 1978

NASA Langley Composites Workshop

TYPICAL THERMAL CONDITIONS IN FREE-BURNING

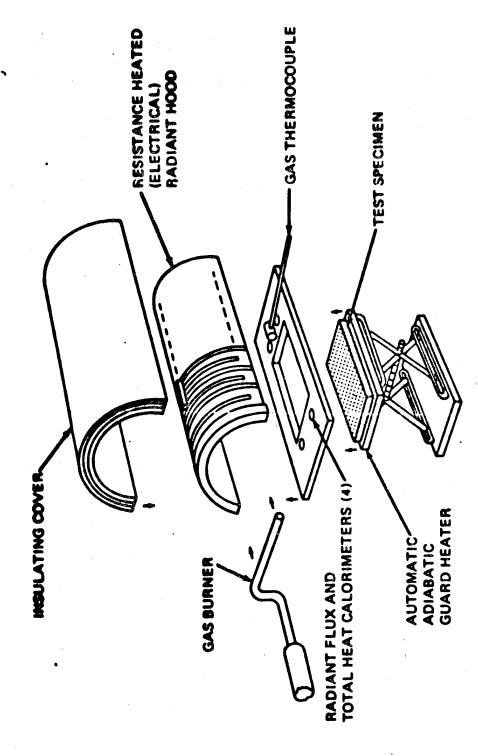
HYDROCARBON POOL FIRES



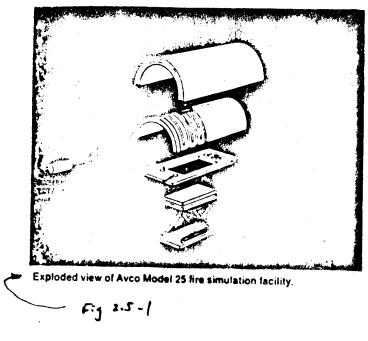


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EXPLODED WIEW OF THE MODEL 25 FIRE SMALLATION FACILITY



FG. 3



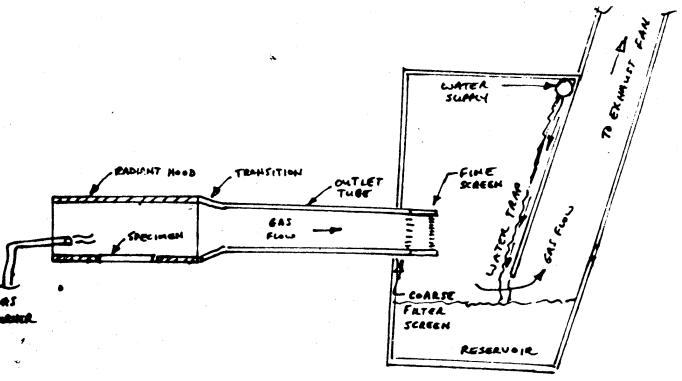


Figure 2.5-2

Model 25 Facility Modified for Fiber Containment

FIRE TEST RESULTS OF GRAPHITE-EPOXY COMPOSITES

IN AVCO'S MODEL 25 FIRE TEST FACILITY

	SPECIMEN NUMBER		
PARAMETER	<u>#153</u>	#4	
MATERIAL DESCRIPTION:		. *	
FIBER	T-300 GRAPHITE	T-300 GRAPHITE	
RESIN	AS 3501-6 EPOXY	AS 3501-6 EPOXY	
MANUFACTURER	HERCULES	HERCULES	
LAMINATION	(<u>+</u> 45,0,90, + 45,0,90) X2	UNIDIRECTIONAL	
SPECIMEN THICKNESS	~ 0.1 INCH	0.125 INCH	
RESIN CONTENT	~ 30%	26%	
THERMAL ENVIRONMENT:		4	
FIRE TEMP.	1850 ⁰ F	1850 ⁰ F	
RADIATIVE HEAT FLUX (1)	9.5 BTU/FT ² SEC	9.5 BTU/FT ² SEC	
CONVECTIVE HEAT FLUX (1)	1.5 BTU/FT ² SEC	1.5 BTU/FT ² SEC	
REMARKS	CONVECTIVE HEAT FLUX OBTAINED FROM A FORCED AIR DRAFTi.e., THERE WAS NO OIL OR GAS BURNER USED FOR THIS SET OF TESTS		
TEST TIME	10 MINUTES	10 MINUTES	
TEST DATA:			
WEIGHT LOSS	63%	46%	
MAXIMUM BACKFACE TEMP	~ 1650°F	1660 ^o F	

NOTES:

⁽¹⁾ AS MEASURED BY RADIOMETER AND CALORIMETER, RESPECTIVELY

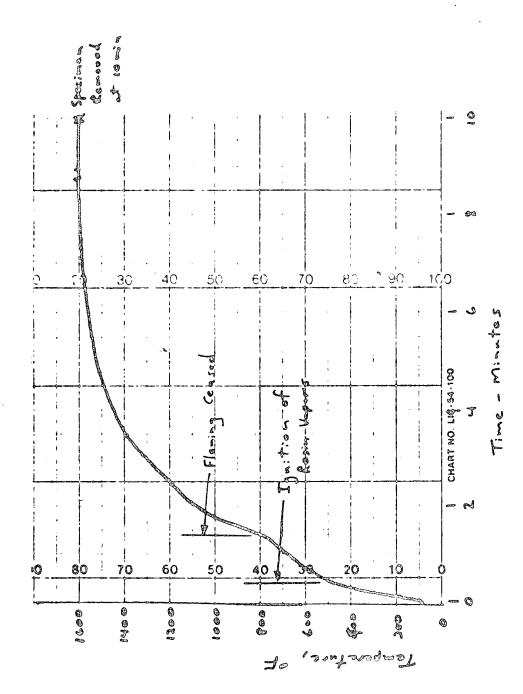
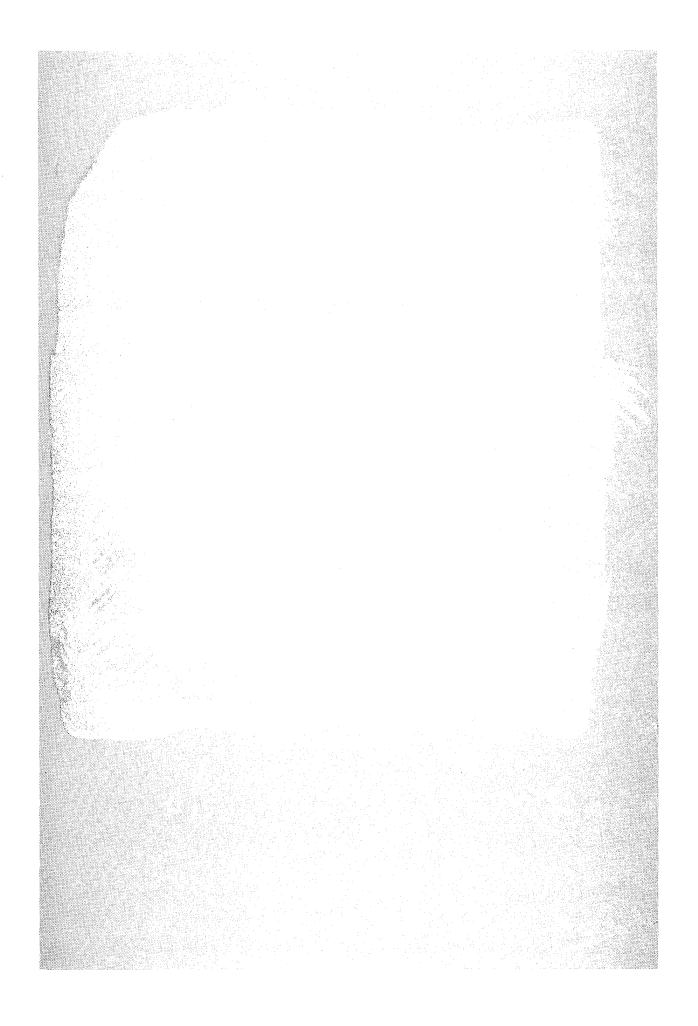
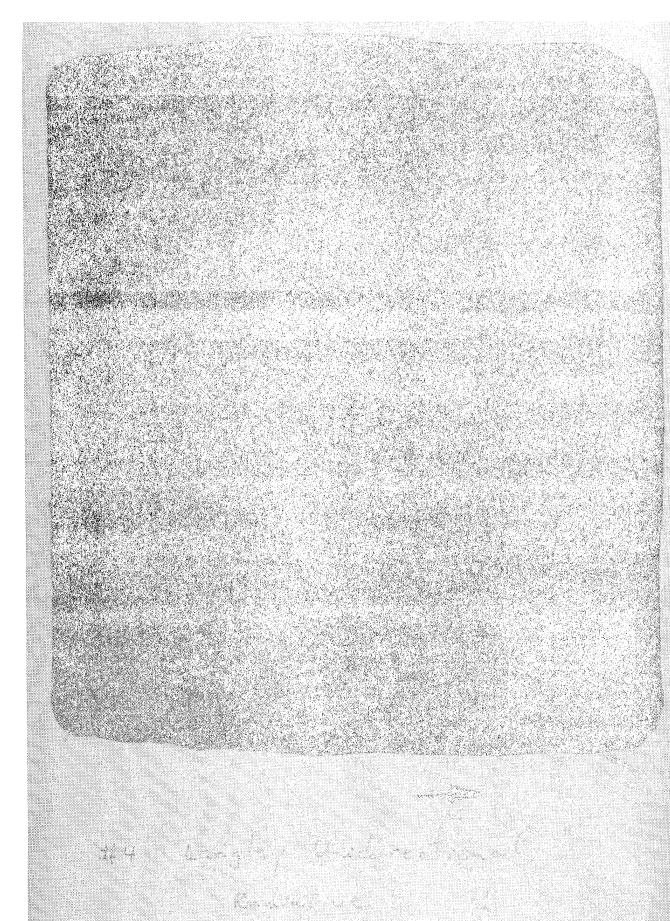


Figure 2.5-3 Backface Temperature Response, Specimen 187





CONCLUSIONS FROM FIRE TEST EVALUATION OF GRAPHITE EPOXY LAMINATES

- 1.) RESIN BURNED OFF IN LESS THAN 3 MINUTES.
- 2.) AFTER RESIN IS BURNED OFF, FIBERS ARE READILY REMOVED. -ESPECIALLY IF MECHANICAL PERTURBATION OCCURS.
- 3.) FIBER RELEASE MORE PRONOUNCED ON CROSS-PLY LAMMATES VS.
 UNIDIRECTIONAL LAMINATES.
- 4.) UNIDIRECTIONAL LAMINATES WARPED DURING TEST
- 5.) ALL LIMINATES SWELLED TO AT LEAST 2X ORIGINAL THICKNESS WITHIN THE FIRST 1-3 MINUTES OF FIRE EXPOSURE.

FIRE TEST FACILITY DEVELOPMENT

- 1.) IMPROVE FIBER COLLECTION TECHNIQUE AND/OR QUANTITATIVE M'MENT OF FIBER RELEASE.
- 2.) ADD SELAS BURNER FOR HIGH \dot{q} c
- 3.) ADD MECHANICAL LOAD CAPABILITY
- 4.) SEAL AIR INGRESS LEAKS
- 5.) INCREASE SPECIMEN OR HOOD SIZE?
- 6.) CUT HOLD FOR BETTER MOVIE ACCESS? VIDEO TAPE?

APPENDIX A

CONVERSION OF MISCELLANEOUS UNITS TO SI UNITS

The International System of Units (SI) was adopted by the Eleventh General Conference on Weights and Measures in Paris, October 1960 . Factors for the conversion of the miscellaneous units used in this document to SI units are given in the following table:

Physical Quantity	Miscellaneous Unit	Conversion Factor (b)	SI Unit
Density	g/cc=g/cm ³ g/ml lb/in ³	10 ³ 10 ³ 2.768×10 ⁴	kg/m3 kg/m3 kg/m3
Energy	in-lb	0.113	J
Flow rate, volume	CFM=ft ³ /min	4.719x10 ⁻⁴	m ³ /s
Heat flux	Btu/ft ² s	1.135x10 ⁴	W/m ²
Length	A	10-10	m
	ft	0.3048	m
	$\mu = \underset{\text{mil}=10}{\text{migron}}$	0.0254	m m
Mass		2.54x10 ⁻⁵	m
Pressure	1b	0.4536	kg
Stress	mm Hg	133.3	Pa
bcress	psi=lbf/in ² kpsi=ksi=10 ³ lbf/in ²	6895	Pa
	Mpsi=Msi=10 ⁶ lbf/in ²	6.895x10 ⁶ 6.895x10 ⁹	Pa
Stress intensity	ksi-in ^{1/2}	1.099x10 ⁶	Pa 3/2
Temperature	°C	°C+273.15	N/m ^{3/2}
	$\circ_{_{\mathbf{F}}}$	Ĭ	K
Thermal efficiency	Btu/lb	(^O F+459.67)/1.8 2324	K
Velocity	ft/s		J/kg
-	knot	0.3048 0.5144	m/s m/s

Amer. Soc. Testing Mater., c. 1977.

b Multiply value given in miscellaneous unit by conversion factor to obtain equivalent value in SI unit (with the exception of temperature).

APPENDIX B

LIST OF ATTENDEES

AKER, Sam C. Bell Helicopter Textron

ACHHAMMER, Bernard G. NASA Headquarters

ALEXANDER, William T. U.S. Army R&T Laboratories

ALLEN, James D. Dr. Fiberite Corporation

BAILEY, William J. University of Maryland

BAUMGARTNER, W. F. Dr. Lockheed - California Co.

BELASON, Bruce E. AVCO Speciality Materials

BERSCH, Charles F. Naval Air Systems Command

BILOW, Norman Dr. Hughes Aircraft Company

BROWNING, C. E. Dr. Wright-Patterson AFB

CHARD, William C. Battelle's Columbus Laboratories

CHASE, Vance A. General Dynamics/Company

CRABIREE, David Northrop Aircraft Company

CREMENS, Walter S. Dr. Lockheed - Georgia Co.

CURLEY, Robert McDonnell Douglas

DELANO, Chadwick Aerospace Systems, Acruex Corp.

DIEFENDORF, R. J., Dr. Renssalaer Polytechnic Inst. DHINGRA, Ashok K., Dr. Du Pont de Nemours & Co.

ECONOMY, James, Dr. IBM Research Laboratory

EDELSTEIN, Marold P. David Taylor Naval Ship R&D

ESTERLING, D. M. JIAFS George Washington Univ.

FANCONI, Bruno, Dr. National Bureau of Standards

FISCHBACH, David B. University of Washington

FOYE, Raymond *U.S. Army R&T Laboratory

FREEMAN, W. T. Vought

FRECHE, John C. NASA-Lewis Research Center

FRIGSTAD, Robert A. 3M Co. 3M Center

GALASSO, Frank United Technologies

GAUCHEL, James V., Dr. DeSoto, Inc.

GAUL, John H. Jr. Dow Corning Corp.

GAULIN, C. A. Aerospace Corporation

GIBBS, Hugh H. Dr. du Pont Experimental Station

GOSNELL, Rex B.
RIGGS Engineering Corp.

GRANDEY, Max F. General Electric Co.

GRIMM, Thaddeus C. McDonnell Aircraft Company

HAMILTON, Robert S. The Carborundum Co.

HANAGUD, S., Dr. Georgia Tech.

HANSEN, Frederick C. NASA-Ames Research Center

HARRISON, Ed General Dynamics/Convair

HENSHAW, J. AVCO Speciality Materials

HERGENROTHER, Karl, Dr. Transportation Systems Center

HOERNSCHEMEYER, D. L. Dr. HITCO

HOFFMAN, Richard E. Hercules Inc.

HOGGATT, John T. Beoing Aerospace Corp.

HOUSTON, D. W. Rockwell

HURT, John Dr. U.S. Army Research Office

JARVIS, Neldon Lynn, Dr. Naval Research Laboratory

KATSUMOTO, M. T. Boeing Commercial Airplane Co.

KOTLENSKY, W. V. Dr. TRW Defense & Space Systems Group

KRAY, Raymond J. Dr. CIBA-GEIGY Corp.

LANDRUM, B. F. CIBA-GEIGY Corp.

LEAL, Joseph R. Celanese Research Company

LEE, David W. U.S. Army R&D Command

LOPEZ, Edward L. Lockheed - California Co.

MANSFIELD, Joseph A. NASA-Ames Research Center

MAY, Clayton A. Lockheed Missiles & Space Co.

MCFERRIN, John H. Union Carbine

MCGANN, Thimothy W. Rockwell International

MCINIYRE, Robert T. The Boeing Vertol Co.

MCKAGUE, Lee General Dynamics

MCMAHON, Paul E. Celanese Research Co.

MOULTON, Richard J. HEXCEL

MROZOWSKI, S.

MUELLER, William A. Jet Propulsion Lab.

MUSSELMAN, Kenneth A., Dr. Naval Surface Weapons Center

NOLAND, James, Dr. American Cyanamid Co.

O'RELL, Michael TRW - Systems

PARKER, John A. NASA-Ames Research Center PAUL, J. T. Hercules, Inc.

PEFBLES, L. H., Jr., Dr. Office of Naval Research

PEPPER, Roger T., Dr. Fiber Materials, Inc.

PETERSON, James M. Boeing Commercial Airplane Co.

PETKER, Ira Composites Horizons

PRESCOIT, Roger Great Lakes Research Corp.

PREWO, Karl M., Dr. United Technologies Research Ctr.

RAMOKALLI, Kumar, Dr. JPL

REARDON, Joseph P., Dr. Naval Research Lab.

RICCITIELLO, S. R. NASA-Ames Research Ctr.

RIEL, Frank J. ROHR

RIGGS, Dennis M., Dr. Army Materials & Mech. Res. Ctr.

SAFFIRE, V. N. General Electric

SANDERS, Harold, Jr. Grumman Aerospace Materials

SANDERS, Robert Rockwell

SCHELL, John T. NASA Marshall

SCHJELDERUP, H. C., Dr. Douglas Aircraft Co.

SCHWEMER, Warren C., Dr. Vought Advanced Technology Ctr.

SCOLA, Daniel A., Dr. United Technologies Res. Ctr.

SERAFINI, Tito T., Dr. NASA Lewis Research Ctr.

SHAFFER, R. C. HITCO Defense Products Div.

SHIPLEY, John L. U.S. Army R&T

SHUFORD, Richard J., Dr. Army Materials & Mech. Res. Ctr.

SIMON, Robert A. Naval Surface Weapons Ctr.

SNYDER, William J., Dr. Bucknell University

SPICER, Herbert C., Jr. Federal Aviation Admin.

STOCKS, Ronald, Dr. CIA OSI/LSD

STREET, Sidney, W. U. S. Polymeric - HITCO

SUBRAMANIAN, R. V. Washington State University

SUNSHINE, Norman B., Dr. Narmco Materials, Inc.

SUPLINSKAS, Raymond J. AVCO Speciality Materials

SVARNEY, Thomas E. George Washington Univ.

TOELLNER, Henry M. McDonnell Douglas

TOMERLIN, R. J. Bell Helicopters - Textron

TRACY, Richard, Dr. LearAvia

VARSI, Guilio Jet Propulsion Lab. VERZINO, W. J. Aerospace Corp.

VOGEL, Lincoln F. University of Pennsylvania

VOLK, Herbert F., Sr. Union Carbide Corp.

WHITSETT, Charles R. McDonnell Douglas Research Lab.

WINTERS, William E., Dr. TRW Equipment

WILLIAMS, Dell NASA Headquarters, RW-3

WITTENWYLER, C. V. Shell Dev. Co.

WOOLEY, John H. Lockheed Calif.

BELL, Vernon L. NASA Langley

BREWER, William D. NASA Langley

PROOKS, William A. Jr. NASA Langley

CHAPMAN, Andrew NASA Langley

CLARK, Ronald K. Dr. NASA Langley

DAVIDSON, John R. NASA Langley

DAVIS, John G., Jr. NASA Langley

DICUS, Dennis L. NASA Langley

ELBER, W. NASA Lengley

HARDRATH, H. F. WASA Langley

HELDEWELLS, Richard R. NASA Langley

HERGENPOTHER, Paul NASA Lengley

JEWELL, R. A. NASA Langley

JOHNSTON, Norman J. NASA Lengley

KING, Chatles B. NASA Langley

LISAGOR, Barry W. NASA Langley MATHAUSER, Eldon E. NASA Langley

NAUMANN, Eugene C. NASA Langley

PASTERNAK, Barbara NASA Langley

PITTMAN, C. M. NASA Langley

PRIDE, Richard A. NASA Langley

RHODES, Marvin NASA Langley

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16. Abstract A hazard which results from accidental release of graphite fibers from composite materials has been identified. The risk resulting from this hazard is being evaluated. In the meantime, NASA has initiated a program to explore alternate materials which eliminate the hazard or reduce the risk. On March 23 and 24, 1978, NASA Langley Research Center sponsored a Modified Composite Materials Workshop. This workshop was intended to display the NASA program on alternate materials and to solicit new ideas for other alternate materials. Working groups were organized to consider six topics: epoxy modifications, epoxy replacement, fiber modifications, fiber coatings and new fibers, hybrids, and fiber release testing. Because of the time required to develop a new material and acquire a design data base, most of the workers concluded that a modified composite material would require about four to five years of development and testing before it could be applied to aircraft structures. However, the Hybrid Working Group considered that some hybrid composites which reduce the risk of accidenta fiber release might be put into service over the near term. The Fiber Release Testing Working Group recommended a coordinated effort to define a suitable laboratory test. That group did not have sufficient time to give careful consideration to the problems of large scale outdoor testing to prove the performance at full scale of proposed alternate materials. Most groups expressed a desire for further interaction with NASA in their technology areas in the future to monitor progress. 12. Key Words (Suggested by Author(s)) graphite fibers; carbon fibers; resin matrices; Unclassified - Unlimited reinforced plastics; hybrid composites;						
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